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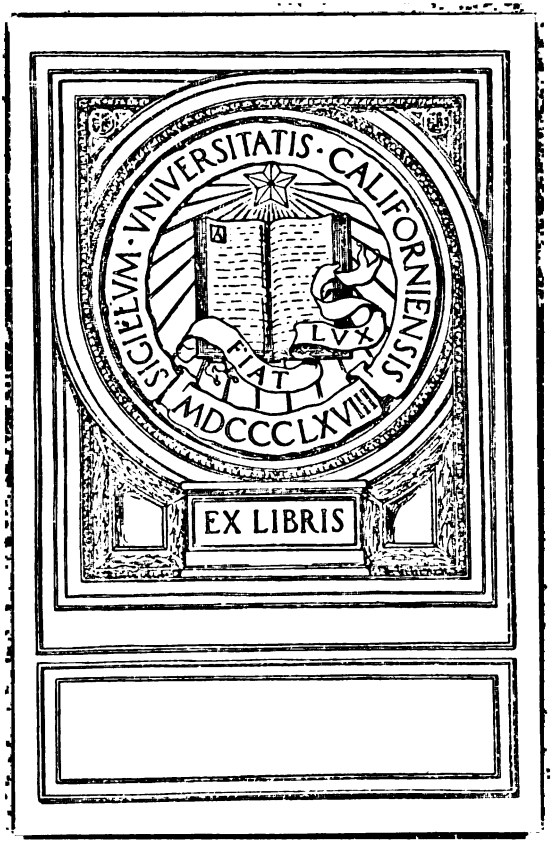
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MONOGRAPHS ON INDUSTRIAL CHEMISTRY
EDITED BY SIR EDWARD THORPE, C.B., LL.D., F.R.S.

THE NATURAL ORGANIC COLOURING MATTERS

THE NATURAL ORGANIC COLOURING MATTERS

BY

ARTHUR GEORGE PERKIN

F.R.S., F.R.S.E., F.I.C.

PROFESSOR OF COLOUR CHEMISTRY AND DYEING IN THE UNIVERSITY OF LEEDS

AND

ARTHUR ERNEST EVEREST

D.Sc., PH.D., F.I.C.

OF THE WILTON RESEARCH LABORATORIES

LATE HEAD OF THE DEPARTMENT OF COAL-TAR COLOUR CHEMISTRY

TECHNICAL COLLEGE, HUDDERSFIELD

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MONOGRAPHS ON INDUSTRIAL CHEMISTRY

Edited by Sir EDWARD THORPE, C.B., LL.D., F.R.S.
Emeritus Professor of General Chemistry in the Imperial College of Science and Technology, South Kensington; and formerly Principal of the Government Laboratory, London

INTRODUCTION

DURING the last four or five decades the Applications of Chemistry have experienced an extraordinary development, and there is scarcely an industry that has not benefited, directly or indirectly, from this expansion. Indeed, the Science trenches in greater or less degree upon all departments of human activity. Practically every division of Natural Science has now been linked up with it in the common service of mankind. So ceaseless and rapid is this expansion that the recondite knowledge of one generation becomes a part of the technology of the next. Thus the conceptions of chemical dynamics of one decade become translated into the current practice of its successor; the doctrines concerning chemical structure and constitution of one period form the basis of large-scale synthetical processes of another; an obscure phenomenon like Catalysis is found to be capable of widespread application in manufacturing operations of the most diverse character.

This series of Monographs will afford illustrations of these and similar facts, and incidentally indicate their bearing on the trend of industrial chemistry in the near future. They will serve to show how fundamental and essential is the relation of principle to practice. They will afford examples of the application of recent knowledge to modern manufacturing procedure. As regards

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their scope, it should be stated the books are not intended to cover the whole ground of the technology of the matters to which they relate. They are not concerned with the technical *minutiæ* of manufacture except in so far as these may be necessary to elucidate some point of principle. In some cases, where the subjects touch the actual frontiers of progress, knowledge is so very recent and its application so very tentative that both are almost certain to experience profound modification sooner or later. This, of course, is inevitable. But even so such books have more than an ephemeral interest. They are valuable as indicating new and only partially occupied territory; and as illustrating the vast potentiality of fruitful conceptions and the worth of general principles which have shown themselves capable of useful service.

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PREFACE.

SINCE the publication in 1874 of Crookes's "Handbook of Dyeing and Calico Printing," in which some space is given to an account of the chemistry at that time known of the natural colouring matters, no volume dealing with this subject in any detail has appeared in the English language.

Indeed, prior to the year 1880, excepting in the cases of Madder and Indigo, very little was known of the chemical structure of these colouring matters, and, in fact, it is only during the last thirty years that sufficient information has been gained to render the publication of a work bearing exclusively on this subject of real value.

In 1900 the first volume of Rupe's well-known handbook "Die Chemie der Natürlichen Farbstoffe" appeared, and, owing to the revival of interest in the investigation of these substances and to the large amount of new knowledge which had rapidly accumulated, a second volume was added in 1909. This handbook has, however, not been translated into English, and as a very considerable mass of new facts have come to light during the past decade, a new treatise on the subject seemed advisable.

The present volume has been compiled with the object of giving as complete an account as possible of the properties of the natural colouring matters, including more particularly a discussion of those facts which have led to a determination of their constitutions. The intention has been to make this book not only of interest to the student but of value as a work of reference to the investigator, and with the latter

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object in view, special attention has been directed, in the case of many of these substances, to the details which are essential for their isolation and purification. Certain chapters are based on articles which have already appeared in Thorpe's "Dictionary of Applied Chemistry".* These have been re-modelled in many cases and enlarged by the addition of such new matter as seemed desirable.

It is well known that the technical value of the Natural Dyestuffs has greatly decreased of late years, and indeed some, which were at one time largely used, have become almost entirely obsolete, at least throughout the Western Hemisphere. Nevertheless, while certain of these are still found to be of some service, though only employed in trifling amount, considerable quantities of others, notably logwood, fustic, Persian berries, and catechu, are in daily use.

The attempts which have been made to utilise the more readily accessible of the naturally occurring colouring matters as starting-points in the building up of synthetic dyes of greater value, have as yet met with comparatively little success, but this field is far from exhausted, and may yet afford results of economical and technical importance.

On the other hand, the employment of these dyestuffs for the colouring of articles of food, of oils and the like, for which, on account of their harmless nature, they are well suited, is extending. This useful application has indeed been recognised for a considerable time as possible, but it is only within recent years, and more especially on the Continent, that any large development has taken place in this direction. In certain of the more important synthetic dye factories, special laboratories have been assigned to the study of this development, and much work has been done both on the economical isolation of certain of these colouring matters in a condition sufficiently pure for use, etc., and on the preparation of soluble derivatives therefrom.

These products, prior to the war, were imported into this

* "A Dictionary of Applied Chemistry." By Sir Edward Thorpe, C.B., LL.D., F.R.S. Longmans, Green & Co., London and New York.

and other countries in considerable amount, and the money value of this trade was large and on the increase.

Apart from these technical considerations, there is hardly a group of substances in the whole range of organic chemistry which offers greater fascination to the purely scientific investigator than the study of the naturally occurring colouring matters and the elucidation of their remarkable relationships to one another.

LEEDS, *October*, 1918.

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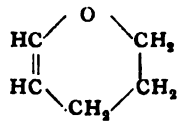

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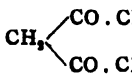

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ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. d. Akad. Krakau	Annalen der Akadamie Krakau.
Annalen	Justus Liebig's Annalen der Chemie.
Annales des Sc. nat.	Annales des Sciences naturelles (*ca.* 1850).
Apoth. Zeit.	Apotheker Zeitung.
Arbeit a. d. K. Gesundht.	Arbeit aus dem Kaiserlichen Gesundheitsamte.
Arch. Internat. Pharm. Ther.	Archives Internationales de Pharmaco-dynamie et de Thérapie.
Arch. Néerland.	Archives Néerlandaises des Sciences exactes et naturelles.
Arch. Pharm.	Archiv. der Pharmazie.
Atti Real. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beiträge f. Wissench. Bot.	Beiträge für Wissenschaft der Botanik.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. Bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. Pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Biochem. J.	The Biochemical Journal.
Bot. Ztg.	Botanische Zeitung.
Brandes' Archiv Apoth.	Rudolph Brandes' Archiv des Apothekervereins im Nördlichen Deutschland.
Buchner's Repert. f. Pharm.	Buchner's Repertorium für die Pharmazie (Munich).
Bull. Soc. chim.	Bulletin de la Société chimique.
Bull. Soc. Ind. Mulh.	Bulletin de la Société industrielle de Mulhouse.
Chem. News	Chemical News.
Chem. Soc. Proc.	Proceedings of the Chemical Society.
Chem. Soc. Trans.	Transactions of the Chemical Society.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.

ABBREVIATED TITLE.	JOURNAL.
Ding. poly. J.	Dingler's polytechnisches Journal.
Edin. New Phil. J.	Edinburgh New Philosophical Journal.
Gazzetta	Gazzetta chimica italiana.
J. (or Jahres.)	Jahresberichte über die Fortschritte der Chemie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society, London.
J. Chim. Med. (or J. de Ch. Med.)	Journal de Chimie médicale de Pharmacie et de Toxicologie.
J. Pharm. Chim. (or Journ. de Ph. et de Chim.)	Journal de Pharmacie et de Chimie.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
Jahrber. d. K. K. Önol. u. pomol.	Jahresbericht der Kaiserlich Königlich önologischen und pomologischen Lehranstalt in Klosternerberg.
Journ. de Chim. Medicale	Journal de la Chimie Medicale.
Journ. Soc. of Arts	Journal of the Society of Arts.
Mitt. K. Tech. Gew. Mus. Wien.	Mittheilungen des Kaiserlichen Königlichen technologischen Gewerbe-Museums in Wien.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
N. Repert. Pharm.	Neues Repertorium für die Pharmazie.
New Zealand J. Sci. Tech.	New Zealand Journal of Science and Technology.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeitschrift für Russland	Pharmazeutische Zeitschrift für Russland.
Phil. Mag.	Philosophical Magazine.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie.
Polyt. Zent.	Polytechisches Zentralblatt.
Pring. Jahrber. f. wiss. Bot.	Pringheim's Jahresbericht für wissenschaftliche Botanik.
Proc. K. Akad. Wetensch.	Proceedings Koninklijke Akademie van Wetenschappen te Amsterdam.
Proc. Roy. Akad. Scien. Amsterdam	Proceedings of the Royal Academy of Sciences, Amsterdam.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Rec. Trav. Chim.	Receuil des Travaux Chimiques des Pays Bas et de la Belgique.
Rend. Acad. Linc.	Atti della Reale Accademia dei Lincei.
Roy. Soc. N.S. Wales	Royal Society of New South Wales.
Scherer's Ann.	Allgemeine nordische Annalen der Chemie, edited by Scherer.
Schweigger's J. Ch. Phys. (or Schweigger Jour. f. Chem.)	Schweigger's Journal für Chemie und Physik.

ABBREVIATED TITLE.	JOURNAL.
Schweiz. Polyt. Zeitschr.	Schweizerische Polytechnische Zeitschrift.
Schweiz. Woch. Chem. Pharm.	Schweizerische Wochenschrift für Chemie und Pharmazie.
Sitzber. d. Kgl. Preuss. Akad. d. Wiss.	Sitzungsberichte der Königlichen Preussischen Akademie der Wissenschaft Berlin.
Sitzber. K. Akad. der Wiss.	Sitzungsberichte der Kaiserliche Akademie der Wissenschaften in Wien.
Trans. Roy. Soc. S. Africa	Transactions of the Royal Society of South Africa.
Vierteljahrsch. Pharm. J.	Vierteljahresschrift für praktische Pharmazie.
Wien Ans.	Anzeiger der Kaiserlichen Akademie der Wissenschaften, Wien.
Zeit. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs-und Genussmittel.
Zeitschr. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. Farb. Text. Chem.	Zeitschrift für Farben und Textil Chemie.
Zeitsch. Physiol. Chem.	Hoppe-Scylers Zeitschrift für Physiologische Chemie.

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ERRATA.

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,,	124,	,,	16,	,,	Saul	,,	Paul.
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INTRODUCTION.

THE employment of natural dyestuffs dates back to remote antiquity, and we have no knowledge when their tinctorial properties were first discovered and what was the original method of their application. It is to be presumed that the first steps in the art of dyeing resulted from the accidental staining of the skin or fabric by a vegetable material, and were followed by the use for this purpose of extracts of this and of other similar products which possessed colour. In this manner certain fairly permanent effects due to a real attraction between colouring matter and fibre would come to light, and a substantive natural dyestuff would thus be revealed. On the other hand, substantive dyestuffs occur but rarely in nature, and it was not until the discovery of the art of mordanting, known, however, at a very early date in Hindustan and the Far East, that any considerable advance in real dyeing became possible. The mordants at first employed consisted evidently of the naturally occurring sulphates of aluminium and iron, the former being the most valuable for this purpose. Indeed Bancroft in his "Philosophy of Permanent Colours" (1813) remarks that the discovery of alum was one of the most important events in the history of dyeing. A method became thus available for the utilisation of the numerous adjective or mordant dyestuffs with which nature abounds, and moreover varied coloured effects of a really permanent character, previously unknown except perhaps in the case of indigo dyed materials, could now be produced by the dyer. A knowledge of the use of these salts gradually spread from India and Persia to Egypt, thence to Greece and Rome, and ultimately farther westward, of which matters an interesting account is given by Bancroft (*loc. cit.*). Important, again, for the progress of dyeing was the discovery of America, which resulted in the introduction into Europe of valuable dyestuffs previously unknown, such as logwood, brazil-wood, and cochineal.

The variety of natural products which have been and still are employed for dyeing is large, though the use of many of these has been confined to the uncivilised or semi-civilised countries in which they abound. Those which have acquired economic importance

are comparatively few in number, and may be said to represent the survival of the fittest since no better natural dyestuffs are known, or are likely to be discovered in the future. These comprise:—

Logwood	Alkanet	Young fustic
Brazil-wood	Cochineal	Quercitron bark
Sanders-wood	Lac-dye	Persian berries
Barwood	Turmeric	Old fustic
Camwood	Annatto	Safflower
Caliaturwood	Orchil?	Indigo
Madder	Weld	Woad?

Without doubt, this list could have been usefully extended in the past by the inclusion of certain of the native Indian dyes, such as Chay root and Morinda root, etc., had better methods of cultivation been adopted and a more exact knowledge of their tinctorial properties been obtained.

Whereas the majority of these dyes, owing to the advent of artificial colours, are now of limited importance, considerable quantities of logwood, old fustic, Persian berries, and catechu still find application, and though the use found for the remainder is trivial in the extreme compared with that of former days, it cannot be said that any have entirely disappeared from the market. A revival indeed of the employment of natural dyes has occurred at the present time, due to the scarcity of the artificial colouring matters, but this cannot be of a permanent character. Owing to the easy solubility of the natural colouring matters, especially in presence of other extractive matter derived from the plant, which permits of their ready absorption by the fabric during the dyeing process, and to the fact that the majority yield with mordants colours of a more or less permanent character, as a class they suffered but little in general estimation during the twenty years which succeeded the advent of the artificial dyes. Madder up to that time the most important of all colouring matters, was, however, soon superseded by the synthesis on a commercial scale of its main colouring matter, and the gradual introduction of the brighter and more easily applied azo dyestuffs caused a steady decline in the employment of other of these natural products. Indigo, the most important survivor of the vegetable group, is now produced artificially, and there can be little doubt that the virtual extinction of the remaining members of this class which still find application is merely a matter of time.

In addition to the commercially important natural dyestuffs, there are a very large number, which on account of their inferior tinctorial

strength, and for other reasons, are now practically unused. Among these are to be found kermes, the oldest dyestuff on record, dyer's broom, green ebony, onion skins, alder bark, saw-wort, and walnut skins, all of which were of service in the past, more especially to the home dyer in whose district they were available. Even at the present day heather and a species of lichen known as "crottle" are still employed in the outlying districts of Scotland and Ireland, and the use of other of these secondary natural dyestuffs may still prevail in like case to a minor extent throughout Europe. Of the Eastern dyestuffs which come under this category there are a considerable variety, including, in addition to those previously mentioned, the root bark of the *Ventilago madraspatana*, the bark of the *Myrica nagi* or *rubra*, the flowers of the cotton plant and of the *Butea frondosa* (Tesu flowers), the *Cedreela toona* and *Thespasia lampas*, Kamala, Waras, pomegranate rind, Lokao, and the buds of the *Sophora japonica*. In certain of our museums, again, specimens of numerous so-called natural dyestuffs are to be found, mostly originating from the East, which merely dye or stain fabrics indefinite shades of a brown or brownish-red colour. Many of these no doubt contain red phlobaphens formed by an alteration of a catechol tannin, whereas probably in others the small amount of dye originally present has suffered decomposition. Though natural products which are, or have been, employed for dyeing fabrics are extremely numerous, they represent but a small portion of those vegetable products in which colouring matter is present. Indeed it is hard to find a plant which, taken as a whole, does not possess the property of dyeing with mordants. That this is the case has been well known for a considerable time, and in the older treatises on dyeing, more especially Bancroft's "Philosophy of Permanent Colours" (1813) and the "Matières tinctoriales" of Leuchs (1829), many plants possessing this character are described. Very generally the mere trace of dye present gives yellow shades on aluminium mordant, and this whilst far too weak in character to have interested the dyer of the past, has now little interest for the chemist owing in general to its identity with one or other of the substances present in some more readily available commercial product.

Though there is no rule by which the existence of a dye in this or that portion of a plant can be predicted with any certainty, the colouring matter in general is most prolific in the leaf or flower, and absent in most cases from the fruit, stem, bark, and root. On the other hand, when present in the latter, these are usually rich in colouring matter, as is the case with Persian berries, the dyewoods,

quercitron bark, and madder. Colourless or yellow flowers capable of dyeing, such as white clover and the yellow primrose, give yellow shades on aluminium mordant, due to the presence of flavone or flavonol glucosides, and these, frequently contained also in red, blue, or violet flowers, are a cause of the green shades they give on aluminium mordant, which otherwise in their absence would be dyed blue as the result of the anthocyanin present. In but rare cases is the yellow dye present responsible for the yellow tint of the flower, for this, usually in the form of glucoside, is more or less colourless. The tint of the latter, in fact, is frequently due to carotin or a similar substance which like this is insoluble in water and devoid of dyeing property. Occasional instances are, however, met with in which the colour of the petal appears to be due to the presence of a yellow acid potassium salt of the flavone glucoside. Very interesting was the discovery by the late Dr. Hugo Müller that flavone is the main constituent of the "farina" or "flour" which accumulates on the leaves of certain varieties of the primula.

As the history of the chemistry of this subject is given in detail later on in respect of each individual dyestuff, many points of considerable interest are purposely omitted in the following brief general statement. During the early part of the last century numerous investigations on the nature and general reactions of the colouring matters present in the natural dyestuffs were carried out, and as the subject was then of considerable technical importance, much space was given to an account of the results in the older manuals of dyeing. These, now difficult of access, and indeed out of print, were Bancroft's "Philosophy of Permanent Colours," 1813; Berthollet, "On Dyeing," translated by Ure, 1824; "Matières tinctoriales," Leuchs, 1829; "Leçons de chimie appliquée à la teinture," Chevreul, 1830; "Traité des matières colorantes," Schützenberger, 1867; and Crookes' "Dyeing and Calico Printing," 1874. Points of interest are also to be found in the still older volume by Hellot on "The Art of Dyeing Wool, Silk, and Cotton," 1789.

The most important of this early work was due to Chevreul, who in 1810 isolated hæmatoxylin from logwood and brazilin from brazil-wood, in 1814 morin from old fustic, and at about the same period luteolin from weld, fisetin (then termed fustin) from young fustic, quercitrin from quercitron bark, and ellagic acid from gall-nuts. In addition to these substances, which are described as crystalline, Chevreul prepared a crude bixin from annatto and proved that a compound capable of developing indigo, rather than indigo itself, is present in the *indigoferæ*. Almost at the same time (1818)

Pelletier and Caventou obtained carminic acid from cochineal, whereas to Robiquet and Colin, in 1826, we owe the first isolation of alizarin from madder, followed a year later by the discovery of purpurin in the same plant. To the first-named chemist is also to be ascribed the detection, in 1849, of orcin from the *Variolaria dealbata*, a variety of lichen employed for the manufacture of orchil. In addition to these colouring matters of commercial importance, others less valuable tinctorially were discovered about this period, among them being berberine (1826), datiscin (1816), gentisin (1827), and rutin (1842). Indeed it may be said that by the end of 1860 few, if any, of the natural tinctorial products readily available had escaped attention. The majority of the colour preparations of these older workers were crystalline, and occasionally chemically pure, as, for instance, the carminic acid of Warren de la Rue (1847), and the methods then devised for their isolation have often proved to be of considerable service to later investigators.

In 1847 a more critical study of madder was commenced by Schunck (Ann. Chem. Pharm., 66, 176), with the result that it was soon evident that this root contained in addition to alizarin and purpurin also a small amount of a complex mixture of yellow crystalline substances now known to be anthraquinone derivatives. Again, it became apparent that certain at least of these compounds were present in the root as glucosides, and eventually the true glucoside of alizarin, the ruberythric acid of Rochleder (1851) termed rubianic acid by Schunck, was isolated in a pure condition. Schunck, from an analysis of the potassium salt of ruberythric acid, deduced for alizarin the formula $C_{14}H_{10}O_4$, and this was subsequently altered by Graebe and Liebermann to $C_{14}H_8O_4$. The preparation of alizarin and purpurin from madder, at best a very tedious process, was simplified to some extent somewhat later by the appearance on the market of preparations designed for calico printing containing the colouring matter in a more concentrated form. Such were the commercial "purpurin" and "green and yellow alizarins" of Kopp (1864), the essential feature in their manufacture being the extraction of the ground root with aqueous sulphurous acid. To within the last fifteen years this operation was still carried out in France, the "purpurin" thus obtained yielding a lake the shade of which was difficult to obtain in other ways. Alizarin, considered to be at first a derivative of naphthalene, was subsequently recognised by Graebe and Liebermann, who employed Baeyer's method of zinc-dust distillation, as a derivative of anthracene, and the suspicion that it was in reality a dihydroxy-anthraquinone was confirmed, as is well known, by its

synthesis in 1868. The production of alizarin on the manufacturing scale no doubt gave hopes of a similar commercial success with other important natural colouring matters, but this, except in the case of indigo, has not been realised, and has been, indeed, unnecessary owing to the production of artificial colours that can be more easily applied to fabrics.

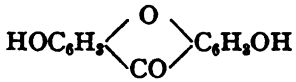
In 1865 Baeyer commenced the long series of researches which led to the synthesis of indigotin, and in 1880 his well-known method for its production from *o*-nitrocinnamic acid was announced. The accounts of these and other researches which have culminated in the manufacture of artificial indigo, are so fully given elsewhere that their repetition here is unnecessary.

Before 1890 little real advance was made in the determination of the actual structure of other commercial natural colouring matters, and, indeed, in many cases their correct formulæ were still in doubt.

Carminic acid, the colouring matter of cochineal, first obtained crystalline by Schützenberger in 1867, had, however, received considerable attention, and the production from it of tri-nitrococussic acid (trinitrocresotinic acid) by Warren de la Rue (1847), of coccinin by Hlasiwetz and Grabowski in 1869, and the bromcarmines by Will and Leymann in 1885, have proved of considerable value to later workers. That progress here was slow can now hardly be wondered at, because of all the natural colouring matters hitherto submitted to exhaustive investigation, carminic acid, perhaps, has appeared the most elusive in disclosing the true nature of its structure. Thus whereas the very able work of Miller and Rohde in 1897 on the bromcarmines suggested the probability that carminic acid was derived from naphthalene, in the same year Liebermann and Voswinkel from a study of its oxidation products preferred then to consider it as a derivative either of hydrindene or bishydrindene, although as the result of further work in 1904 a naphthacene quinone constitution appeared more probable to these authors. Finally, Dimroth (1909), who studied the more gentle degradation of carminic acid, although at first inclined to regard this colouring matter as a naphthalene compound, has, after a series of brilliant investigations (1913), described in the sequel, proved that it is derived from anthraquinone and that both the kermessic acid of kermes and laccainic acid of lac dye contain a similar nucleus.

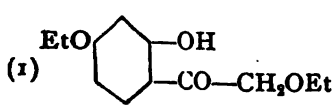
An interesting, though now unimportant, Indian pigment is the Puiri or Indian yellow, a compound deposited from the urine of cows fed on the leaves of the mango tree, and which is the source of the somewhat feeble dye euxanthone. Euxanthone, though of little

interest to the dyer, is historically important in that it was the first of the many natural yellow dyestuffs of which the constitution was determined. A study of this compound by Baeyer in 1870 indicated that it was derived from benzophenone, and, largely as the result of his work, Salzmann and Wichelhaus, seven years later, assigned to it the constitution of a dihydroxy-diphenylene ketone oxide—



Diphenylene ketone oxide, subsequently termed xanthone by v. Kostanecki, was discovered by Kolbe and Lautermann in 1860, who prepared it by the interaction of phosphorus oxychloride and sodium salicylate, though the method devised by the late Sir W. H. Perkin in 1883, which consists in distilling acetic anhydride and salicylic acid, is the most convenient. The products of the hydrolysis of euxanthone are resorcin and hydroquinone carboxylic acid, and by a reversal of this process, that is distilling these substances with acetic anhydride, euxanthone was synthesised by Graebe (1889) and later by v. Kostanecki and Nessler (1891).

The commencement of a new era in the investigation of the natural yellow colouring matters dates from the patient study by Herzig of quercetin (1884), derived from quercitron bark, and fisetin, which is present in young fustic. Although the older formula $C_{24}H_{16}O_{11}$, assigned to quercetin by Liebermann and Hamburger in 1879, was employed in his earlier papers, $C_{15}H_{10}O_7$ was ultimately (1891) proved to be correct. It was subsequently pointed out by Perkin and Pate (1895) that quercetin, fisetin, and other yellow colouring matters yield with acids well-defined salts, the analysis of which indicates with some certainty their molecular weight, as in the case of quercetin which forms salts of the type $C_{15}H_{10}O_7HCl$. Of these two colouring matters Herzig first in 1891 determined the constitution of fisetin; this resulted from a study of the products (fisetol diethyl ether and protocatechuic acid diethyl ether) which he obtained by the gentle hydrolysis of fisetin tetraethyl ether. The fact that fisetol proved to possess the constitution (1)



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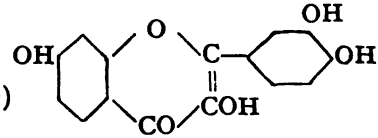
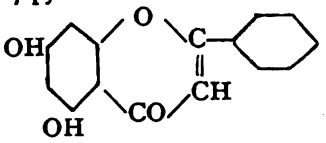


led to the conception that fisetin was in reality the tetrahydroxy phenyl pheno γ-pyrone (2). Quercetin by analogy was represented

as hydroxy fisetin. About the same period (1893) v. Kostanecki submitted to examination chrysin, $C_{15}H_{10}O_4$, a very feeble colouring matter, which Piccard, in 1864, had isolated from the buds of the common poplar. From the properties of this substance and the fact previously observed by Piccard that when hydrolysed it yields acetophenone and phloroglucinol, v. Kostanecki represented it as a dihydroxy phenyl pheno γ-pyrone.



Such a compound on hydrolysis would be expected to give, first, trihydroxy benzoyl acetophenone (1)—

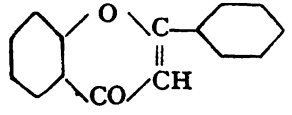
(1) $(OH)_3C_6H_2CO : CH_2COC_6H_5$

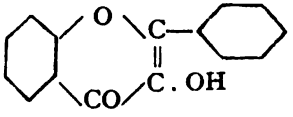
(2) $(OH)_3 . C_6H_2 . CO . CH_2 : COC_6H_5$

and then acetophenone, and phloroglucinol carboxylic acid, the latter subsequently passing into phloroglucinol. On the other hand, the hydrolysis could evidently also take place in another manner (2) with formation of phloracetophenone and benzoic acid, and indeed phloroglucinol and acetic acid, derived from the former, and benzoic acid are also obtained from it in this way.

An intefesting fact observed by v. Kostanecki with chrysin and euxanthone, and by Herzig with quercetin, is that when alkylated with alkyl iodides in the well-known manner the hydroxyl in the ortho position to the carbonyl group is not attacked. Again, the alkylated product, though still containing a free hydroxyl group, is insoluble in aqueous alkali, but gives by means of alcoholic potash a potassium salt which is hydrolysed by water. This behaviour is to a certain extent possessed by all hydroxyketones, and is evidence of an hydroxyl in this position. Perkin has shown, however, in the case of luteolin, quercetin, and the analogously constituted colouring matters myricetin and quercetagetin, that by employing excess of the reagents fully alkylated products can be obtained, and this no doubt will generally prove to be the case.

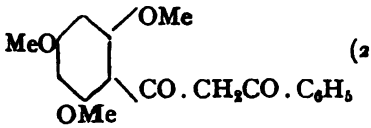
v. Kostanecki designated the mother substance of chrysin flavone (1), whereas the mother substance of fisetin which contains a hydroxyl attached to the γ-pyrone nucleus he termed "flavonol" (2)—

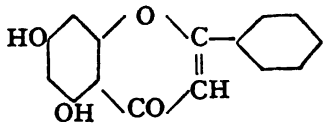
(1) 

(2) 

From the period of 1895 onwards, a considerable number of natural yellow colouring matters have been examined, many of which have been proved to belong to the flavone or flavonol groups, and there can be no doubt that of all the natural dyes, these are much the most widely distributed in nature.

In 1898 Emilewicz, v. Kostanecki, and Tambor announced the synthesis of chrysin, employing for this purpose a series of reactions which represent a reversal of the scheme of hydrolysis outlined above. Thus ethyl benzoate condensed with phloracetophenone trimethyl ether gives 2 . 4 . 6 trimethoxybenzoylacetophenone (1), and this by treatment with hydriodic acid is demethylated, and passes into chrysin—

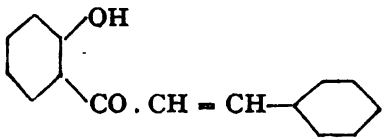
(1) 

(2) 

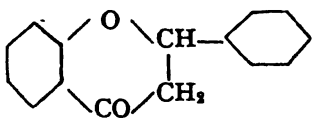
Other methods of synthesis were subsequently applied to chrysin by v. Kostanecki and his co-workers, and in 1899 flavone itself was prepared, followed in 1900 by apigenin (parsley) and luteolin (weld). Somewhat later a method was devised for the artificial preparation of flavonols, and in 1904 fisetin, quercetin, and kaempferol were synthesised by v. Kostanecki and his co-workers, morin being similarly obtained in 1907.

The course of the reactions employed may be illustrated as follows:—

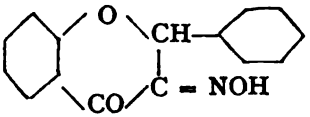
When *o*-hydroxyacetophenone is condensed with benzaldehyde 2 hydroxybenzilidene acetophenone (2 hydroxy chalkone) is obtained—



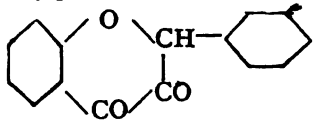
This on boiling in alcoholic solution with dilute sulphuric acid by absorption and elimination of water is converted into dihydroflavone (flavanone)—

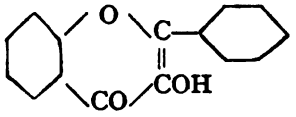


By the action of amyl nitrite and hydrochloric acid iso-nitrosoflavone is produced—

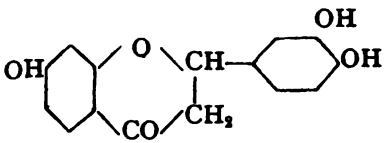


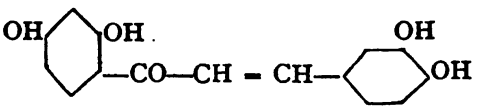
and this dilute sulphuric acid converts into the ketone (1), which subsequently passes into the flavonol (2)—

(1) 

(2) 

Interesting is the fact pointed out by Perkin and Hummel in 1904 that a chalkone and flavanone exist side by side as glucosides, and to a small extent in the free condition, in the flowers of the *Butea frondosa.* These compounds which are named Butin and Butein possess the following constitutions:—

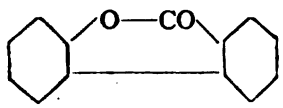


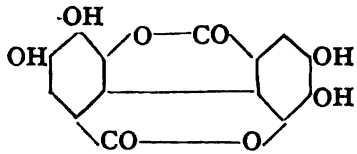


and were synthesised in the form of their trimethyl ethers. Thus resacteophenone monomethyl ether, condensed with protocatechuic aldehyde dimethyl ether forms butein trimethyl ether, and from this the corresponding butin derivative is readily produced by the action of dilute alcoholic sulphuric acid.

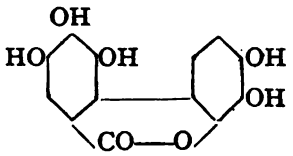
A colouring matter known for many years past, and, in fact, among those examined by Chevreul, is ellagic acid, which though possessing somewhat feeble dyeing properties, gives a very fast shade on a chromium mordant. In the form of ellagitannic acid, it appears to be present in all plants which yield ordinary gallotannin, and is produced in considerable amount when certain tannin extracts, such as those of divi-divi and myrobalans, are subjected to fermentation. Merklein and Wöhler assigned to it, in 1845, the formula $C_{14}H_6O_8$, and it is interesting as the first natural yellow colouring matter to have been synthetically prepared. This was accomplished by Löwe in 1868, who obtained it as a product of the interaction of gallic and arsenic acids, though since then other and better oxidation processes have been devised. Whereas Schiff, as early as 1879, suggested two

constitutions for ellagic acid, one of which is now known to be correct, it was considered by Barth and Goldschmiedt, in the same year, that as ellagic acid when distilled with zinc-dust yields fluorene, it is most probably a fluorenone derivative. Graebe, however, in 1903 pointed out that diphenyl-methylolid (1) treated in this way gives fluorene, and accordingly again proposed the constitution for ellagic acid (2) given in Schiff's paper and referred to above.

(1) 

(2) 

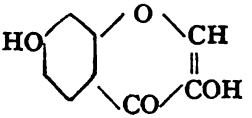
That this is correct was established by Perkin and Nierenstein in 1905, who pointed out that the first product of the hydrolysis of ellagic acid is in reality pentahydroxy-diphenyl-methylolid—



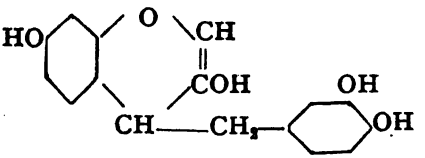
Though ellagic acid is at present the only known naturally occurring member of this group, other hydroxy derivatives of diphenyldimethylolid can be obtained, by the oxidation of hydroxybenzoic acids other than gallic acid, and by the more energetic oxidation of gallic acid itself.

For several years after the time of Chevreul little work of importance was carried out with hæmatoxylin, the colouring principle of the commercially important logwood, though in 1842 Reim proposed for it the formula $C_{16}H_{14}O_6$, which is now known to be correct. Brazilin, the very similar colouring principle of brazil-wood, was examined by Liebermann and Burg in 1876, and the formula $C_{16}H_{14}O_5$ assigned to it, and the many properties it possesses in common with hæmatoxylin indicated its probable relationship to this latter substance. This, as the result of the work of W. H. Perkin (junr.) and his pupils, has ultimately proved to be the case. It had long been known that hæmatoxylin and brazilin were not the actual colouring matters of logwood and brazil-wood, but that to develop this property an oxidation ("ageing") process was necessary. Hæmatoxylin thus yields hæmatein, as shown by Reim in 1871, and that brazilin behaves in the same way with formation of brazilein was pointed out by Liebermann and Burg in 1876. These substances were subsequently,

in 1882, isolated in the pure crystalline condition by Hummel and A. G. Perkin, and from the fact that they, respectively, possessed the formulæ $C_{16}H_{12}O_6$ and $C_{16}H_{12}O_5$, their simple relation to hæmatoxylin and brazilin appeared evident. The study of the constitution of these compounds received its first impetus from the work of Schall and Dralle in 1888, who, by the more energetic oxidation of an alkaline solution of brazilin with air, obtained β-resorcylic acid and a substance which Schall in 1894 considered was the pheno γ-pyrone derivative (dihydroxychromone)—

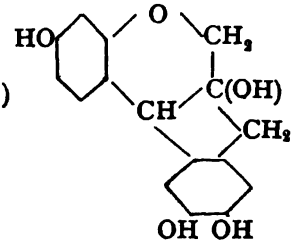


That this supposition was correct was proved by Feuerstein and v. Kostanecki in 1899, and this in conjunction with the fact that Herzig, in 1898, and Gilbody and Perkin, almost simultaneously, had obtained evidence in this compound of a catechol nucleus, led the former investigators to suggest the following as the formula for brazilin :—



In 1899 there appeared the first of an elaborate series of papers by W. H. Perkin and his pupils on the constitution of hæmatoxylin and brazilin, and as a result an important series of acids obtained from both brazilin trimethyl ether and hæmatoxylin tetramethyl ether by oxidation were described. The constitutions of these acids was determined by synthesis, and these results in the face of alternative suggestions by v. Kostanecki and Lampe (1902) and Herzig and Pollak in 1906, resulted in 1908 in the formulæ of Perkin and Robinson for both brazilin (1) and hæmatoxylin (2) which are now accepted as correct—

(1)



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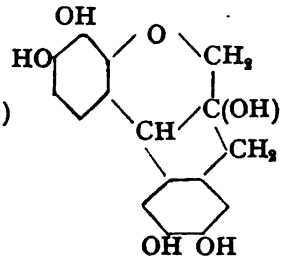
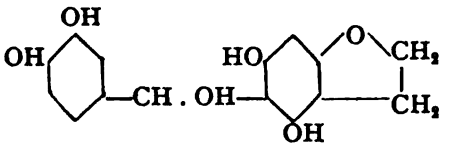


Of interest is the *Hæmatoxylon africanum* more recently discovered in Africa by Pearson, which differs from the *Hæmatoxylon campeachianum* (logwood) in that in place of the hæmatoxylin present in the latter wood, it contains a small amount of a red colouring matter, which judging by its properties, is brazilin itself (A. G. Perkin, private communication).

Though more allied to the tannins, and, indeed, itself largely employed in the tanning of leather, catechu is of considerable service for dyeing purposes, due to an alteration during these processes in the catechin it contains. Catechin was first isolated in 1832 by Nees van Esenbeck, but its true formula, $C_{15}H_{14}O_6$, was only correctly ascertained in 1902 by v.. Kostanecki and Tambor, and Perkin and Yoshitake simultaneously. At the same time the latter authors observed that the catechins of Gambier catechu, and Acacia catechu, though isomeric are distinct substances, that present in the latter being now termed aca-catechin. Whereas Perkin suggested that these catechins were probably reduction products of quercetin, which is always associated with them in the plant, v. Kostanecki and his co-workers produced evidence of a cumaran nucleus in catechin and considered the following expression to be more correct :—

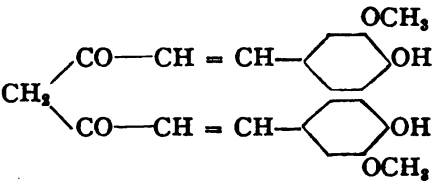


A synthesis catechin compound has not yet been effected, and further work appears necessary to confirm the above formula; moreover, an explanation is still required of the nature of the interesting change by which catechin so readily yields catechutannic acid, the true tanning principle.

As already indicated, the natural substantive dyestuffs comprise but a small group, and have always been of somewhat minor importance, owing to the fact that the shades they yield are either extremely fugitive, or less permanent than those obtainable by other methods. Among these are to be found safflower, annatto, barberry, turmeric, and the insoluble red woods, sanders-wood, barwood, camwood, and caliatur-wood, and it is of interest to note that these latter and also turmeric possess in addition to their substantive character the property of dyeing with mordants.

Of the members of this class the main interest has hitherto centred round turmeric, whose colouring matter, curcumin, was

first isolated by Vogel in 1842. Though obtained crystalline by Daube in 1870 it was not until 1897 that Ciamician and Silber ascertained that its molecular weight is represented by $C_{21}H_{20}O_6$ rather than by the older expression $C_{14}H_{14}O_4$. The problem of its constitution was more recently attacked (1910) by Melobedzka, v. Kostanecki, and Lampe, and there is now little doubt that this colouring matter is an unsaturated β-diketone of the following formula :—



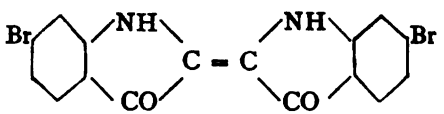
Safflower, at one time highly esteemed as the source of a very beautiful though expensive and fugitive shade of red, whilst still employed in the East, is extinct as a commercial dyestuff in this country. It contains both a red and yellow colouring matter; the latter of little interest, though both have been detected as the cause of the red and yellow dye of certain Egyptian mummy cloths. Carthamine, the red colouring matter first isolated by Schlieper in 1846, received little attention until 1910, when Kametaka and Perkin succeeded in obtaining it in a crystalline condition. Though possessing a more complex formula than curcumin, a certain resemblance exists between these colouring matters, as regards the simple nature of their decomposition products, and there is reason to suppose that they may be structurally related. Definite evidence, however, of the constitution of this latter, of the bixin of annatto still employed in this country for colouring foodstuffs, and of the santalin of sanderswood is still lacking, although the recent work of Cain and Simonsen (1912) has added considerably to our knowledge of this latter compound.

An elucidation of the true nature of the chemistry of the natural indigo process, long overdue, has been rendered clear by the researches of Hoogewerff and ter Meulen. Though Schunck in 1858, as is well known, by his work on woad and the *Polygonum tinctorium*, established in this connection points of considerable importance, his indican, though rich in colouring principle, was amorphous, and of an unstable nature. On the other hand, there is evidence that the colouring principle of woad which he describes is distinct from that present in the *indigoferæ* and the *Polygonum tinctorium*, and, owing to its instability, has hitherto

baffled all attempts to isolate it in a pure condition. It has now been ascertained that pure indican derived from the *indigoferæ*, and which is in reality a glucoside of indoxyl, crystallises readily, and is quite stable in ordinary circumstances, though by the action of dilute acids and of a special ferment present in the plant, it is readily hydrolysed with formation of glucose and indoxyl. By means of a very simple method devised by Perkin and Bloxam in 1907 very large quantities of indican can be readily isolated, and its use has permitted the study in considerable detail of this interesting glucoside.

Closely connected with indigo, as is now proved to be the case, is the so-called purple of the ancients, also known as Tyrian purple, for many ages probably the dye most esteemed above all others. The colouring matter exists in the reduced condition, in very small amount in certain molluscs, as a yellowish-green fluid or solution, which on exposure to air rapidly develops a purple colour. The process by which it was applied to fabrics by the ancients is unknown, but it probably consisted in breaking up the molluscs under water and employing the supernatant liquid for dyeing. According to Crookes ("Calico Printing," 11) molluscs of this character were employed for dyeing purposes in Bristol about 1663. The subject appears to have been first chemically investigated by Bizio in 1833, and the result of this and of later investigations pointed to a considerable resemblance between this colouring matter and indigotin. Schunck in 1879 described in detail the properties of this substance of which from 400 molluscs he obtained 7 milligrams and was successful in obtaining it in a crystalline condition by sublimation.

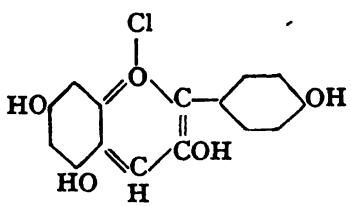
To those who have examined these animals, the difficulty and unpleasantness involved in obtaining a sufficient amount of the colouring matter for investigation appeared almost unsurmountable, but these were overcome with consummate skill by Friedländer in 1906. As the result of this work, which is described in detail in the following pages, Friedländer ascertained that this colouring matter contains bromine and is in reality a dibromindigotin of the constitution—



Of special interest in recent years has been the results of the investigations of Willstätter with Everest (1913) and others on the nature of the red and blue colouring matters of flowers and of fruits which are termed anthocyanins. Though in the past certain berries

containing this class of substances have been employed to a slight extent for dyeing with mordanted fabrics, and it has been known that red and blue flowers give in the same way bluish or more generally greenish shades on aluminium mordant, these colours are fugitive and the subject has hitherto possessed more interest for the biochemist than for the dyer. Beyond the determination of the general properties of these colouring matters, and the fact that whereas blue flowers contain them in a neutral, and red flowers in an acid condition, no evidence of importance as to their structure had been forthcoming until the work of Willstätter and Everest on the blue colouring matter of the corn-flower appeared. As a result of this and later investigations, it is now known that these anthocyanins are always present in the plant as glucosides, and that from these by hydrolysis with acid the free colouring matter termed an anthocyanidin may be isolated in the form of its oxonium salt. Both classes of compounds are crystalline and are not so unstable as their behaviour in the coloured petal would lead one to expect. These compounds are in reality derivatives of benzopyranol and thus are closely connected with the flavones, or flavone glucosides, of which they may be regarded as reduction products. This relationship will be evident on comparing the formula of Pelargonidin (from the *Pelargonium zonale*) as hydrochloride (1) 3 . 5 . 7 trihydroxy 2 *p*-hydroxy phenyl 1 . 4 benzopyranol anhydro hydrochloride with the flavonol kaempferol (*Delphinium consolida*) (2).

(1)



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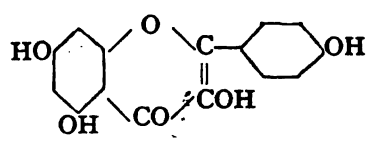


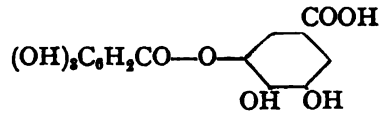
A detailed description of these interesting compounds will be found in a later chapter.

The tannins, at one time employed to a considerable extent in the production of a black or grey colour on fabrics, by means of iron salts, and which even now take part in the black dyeing of silk, are distinct from and, indeed, are not usually classified among dyestuffs.

This arises from the fact that, except in the case of the iron mordant, they do not, as a rule, dye fabrics which have been mordanted with the other metallic compounds used in practice, though, on the other hand, gallotannin is remarkable in that with titanium mordant it produces a bright yellow colour. Whatever view may be taken on this point, tannins are so largely employed as assistants in the dyeing operation, as for instance in the fixation of basic colours on cotton, and appear generally to bear some relationship to the yellow colouring matters with which they are usually associated in the plant, that their description naturally falls within the scope of a work of this character. Perkin, indeed, has pointed out that, in those cases which have been investigated, the tannin or tannin principle, or should there be two, one of these and the yellow colouring matter of the plant, contain either identical phenolic nuclei or at least one phenolic nucleus in common. Thus gallotannin appears to invariably accompany myricetin (pyrogallol nucleus) and a catechol tannin, quercetin (catechol nucleus), whereas catechin and quercetin and cynanomaclurin and morin respectively occurring together contain identical phenolic nuclei.

Though the tannins are very widely distributed in nature, and by their general reactions can be grouped into three main classes, our knowledge of these compounds is slight, except as regards gallotannin. Löwe in 1867 and Schiff in 1871 claimed to have synthesised this compound, and the latter chemist proposed for it the digallic acid structure which was generally accepted for many years. It is now known as the result of the work of Walden (1899) and others, that Schiff's synthetical product, whatever it may have been, is quite distinct from the natural tannin. Among the various suggestions subsequently made as to the constitution of gallotannin, that of Nierenstein, who considered it to consist of a mixture of digallic and leucodigallic acids (1907), appeared most plausible, and indeed in 1910 this author described the preparation of digallic and in 1912 that of leucodigallic acid from gallotannin. In 1912 again Nierenstein came to the conclusion that gallotannin is more complex than he had previously supposed, and that it may consist of a polydigalloyl leuco digalloyl anhydride. Fischer and Freudenberg, however, in 1912 took an entirely different view of the constitution of tannin, and proved that the pure substance when hydrolysed with acid, always gives in addition to gallic acid a small amount of glucose. As a result they consider gallotannin to be a compound of dextrose with five molecules of *m*-digallic acid of the nature of a pentacetyl derivative, which will not only account for its very high molecular weight

but also for its optical activity. These chemists were successful in synthesising both *p* and *m*-digallic acids of which the latter is concerned in the structure of tannin—

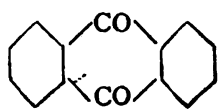


and among the many interesting proofs given in their elaborate work on this subject for their suggested constitution of gallotannin is their synthesis of penta-penta-methyl digalloyl glucose. This though differing slightly in optical activity from the penta-methyl gallotannin of Herzig (1905) very closely resembles it, and there can be little doubt the difference observed is due to the fact that both products contained a mixture of stereo-isomerides.

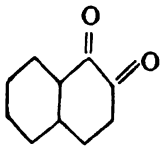
In concluding this brief sketch of the work which has been carried out upon the more important natural dyestuffs, it is hardly necessary to point out that the subject, even in its main features, is far from being exhausted. Not only is this so in respect of the dyes already enumerated, and with those of unknown constitution which are described later on, but in addition there exist without doubt, more especially in certain flowers, numerous natural colouring matters, evidently members of new chemical groups, which yet remain to be isolated. From a study of these no direct technical advantage can be anticipated, but on the other hand an elucidation of their nature will not only assist the biochemist in the problems he has to face, but will add materially to our present knowledge of the effect of constitution on colour.

In the succeeding chapters the natural dyestuffs are grouped according to the constitution, where known, of their main tinctorial constituents, and where members of two widely distinct groups, as for instance, those derived from flavone and anthraquinone, exist side by side in the same plant, the description of the plant will be found under that heading which from its present or past uses appears the more suitable.

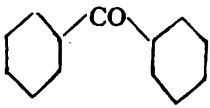
The present known chemical groups to which the natural dyestuffs belong are given below, in the order in which the subject is treated in this volume :—

ANTHRAQUINONE 

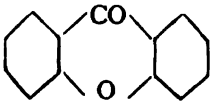
NAPHTHOQUINONE



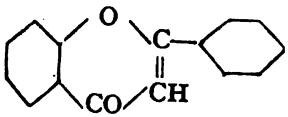
BENZOPHENONE



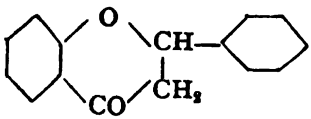
XANTHONE



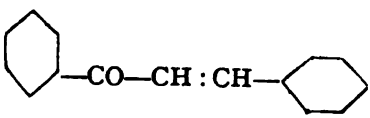
FLAVONE



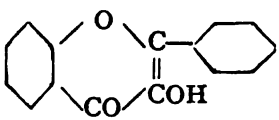
FLAVANONE



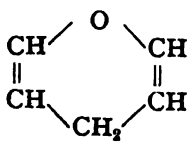
CHALKONE



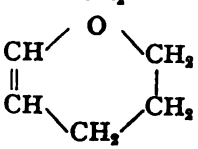
FLAVONOL



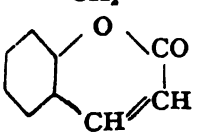
γ-PYRANE



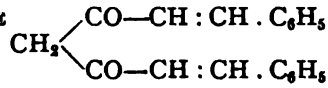
DIHYDROPYRANE



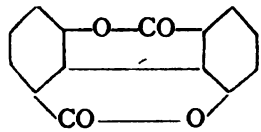
COUMARIN



DICINNAMOYLMETHANE

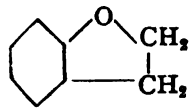


DIPHENYLDIMETHYL-OLIDE

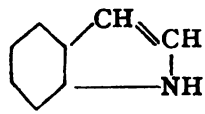


TANNINS

CUMARANE

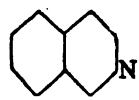


INDOLE



Lichen acids and colouring matters derived therefrom.

ISOQUINOLINE



Colouring matters of unknown constitution.

CHAPTER I.

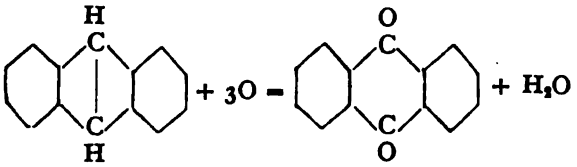
THE ANTHRAQUINONE GROUP.

Anthraquinone—Madder—Chay Root—Species of Galium—Munjeet or *Rubia cordifolia*—*Rubia khasiana*—*Rubia sikkimensis*—*Morinda citrifolia*—*Morinda umbellata*—*Morinda longiflora*—Rhubarb—*Rumex echlonianus*—*Rumex nepalensis*—Senna Leaves—*Rhamnus frangula*—*Polygonum cuspidatum*—Aloes—Goa Powder—*Anchusa tinctoria*—*Onosma echoides*—*Ventilago madraspatana*—Cochineal—Lac Dye—Kermes.

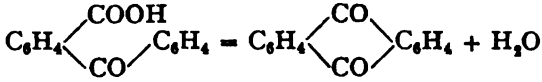
ANTHRAQUINONE.

THE most typical methods for the formation of anthraquinone are :—

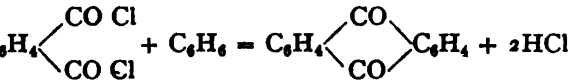
(*a*) The oxidation of anthracene—



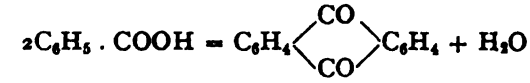
(*b*) Treatment of *o*-benzoyl benzoic acid with sulphuric acid (Liebermann, Ber., 1874, 7, 805; W. H. Perkin, Chem. Soc. Trans., 1891, 59, 1012)—



(*c*) Interaction of phthalylchloride and benzene in the presence of aluminium chloride (Friedel and Crafts, Ann. de Chimie, (6), 1, 523)—

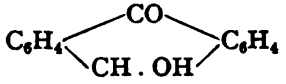


(*d*) Distillation of benzoic acid with phosphorus pentoxide (Kekulé and Franchimont, Ber., 1872, 5, 908)—



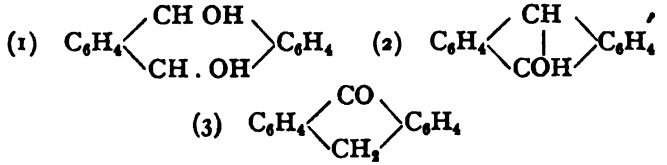
Of these methods (*a*) is the only one suitable for the commercial preparation of anthraquinone, whereas those of the type of (*c*) and

(*d*) have been adapted for pure and applied syntheses of numerous hydroxyanthraquinones. The hydroxyanthraquinones, like anthraquinone itself, by distillation with zinc-dust are reduced to anthracene, and on short digestion with zinc-dust and alkali give unstable alkali salts of hydroxy oxanthranols (Graebe and Liebermann, Annalen, 160, 126)—

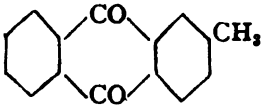


which in solution readily absorb oxygen from the air with regeneration of the colour of the alkali salt of the unreduced substance. These two reactions are typical of hydroxyanthraquinones and are of service for their detection in nature.

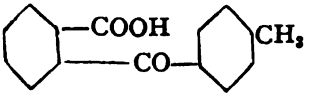
By further reduction oxanthranol passes into the dihydroxy compound (1), which loses a molecule of water with formation of anthranol (2), a compound which also exists in the isomeric form (3). Anthranol is best obtained by the action of tin and hydrochloric acid on anthraquinone in boiling acetic acid solution (Liebermann and Gimbel, Ber., 1887, 20, 1854)—



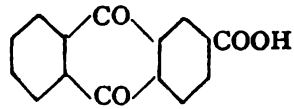
Natural anthraquinone colouring matters are accompanied in many instances by hydroxy α or β-methylanthraquinone derivatives which possess little or no tinctorial property. Of these the hydroxy β-methyl anthraquinones appear to be the most prolific. β-methyl anthraquinone, melting-point 175—177°, may be prepared by the oxidation of β-methyl anthracene, and occurs as a by-product in the manufacture of anthraquinone from crude anthracene (Perkin and Cope, Chem. Soc. Trans., 1894, 65, 843)—



For commercial purposes it is, however, more easily prepared by the interaction of phthalic anhydride and toluene, in which case *o*-toluylbenzoic (1) acid is probably an intermediate product—



(Bücherer, Lehrbuch der Farbenchemie, 1914, 322). By distillation with zinc-dust it yields β-methylanthracene, melting-point 207°, and by oxidation with chromic acid β-anthraquinone carboxylic acid—



melting-point 290—292°. α-Methylanthraquinone, a much less well-known substance, is obtained by the oxidation of α-methylanthracene and melts at 166—167° (Birukow, Ber., 1887, 20, 2070). The corresponding anthraquinone α-carboxylic acid melts at 293—294° (Blumenfeld, Ber., 1897, 30, 1115), whereas α-methyl anthracene itself according to Birukow melts at 199—200°. Hydroxy-methyl-anthranols frequently occur in nature, usually side by side with methyl hydroxy-anthraquinones. They are devoid of tinctorial property, and on gentle oxidation, preferably in acetic acid solution with chromic acid, are converted into the corresponding methylanthraquinone compounds.

MADDER.

Madder is the ground root of the *Rubia tinctorium* (Linn.) which has been cultivated for dyeing purposes from a remote antiquity, so remote indeed that one is unable to say with certainty in which countries it originated. It is known to have been employed by the ancient Egyptians, Persians, and Indians, probably by the last in the first instance, and more recently by the ancient Greeks and Romans. About the time of the Crusades the cultivation of madder was introduced into Italy and probably also into France. The Moors cultivated it in Spain, and during the sixteenth century it was brought to Holland. Colbert introduced it into Avignon in 1666, Frantzen into Alsace in 1729, but only towards 1760—1790 did it become important. During the wars of the Republic, its cultivation was largely abandoned, and only after 1815 did this again become regular.

Owing to the beauty and fastness of the tints it yields, and the range in colour that can be produced from it by a variation in the mordant, it was considered until recently as perhaps the most important of all dyestuffs. Although its commercial value has been greatly reduced through the introduction of artificial alizarin, it has still considerable scientific interest.

The plant is an herbaceous perennial belonging to the natural family of the *Rubiaceæ*, and its valuable portion is entirely the root, which is usually of considerable length but does not exceed an

ordinary slate pencil in thickness. Old roots are richer in colour than young ones, and the plant is consequently left in the soil for at least eighteen and sometimes for twenty-eight months. When removed it is usually washed with water, allowed to dry in the sun or artificially by means of kilns, then finely ground and packed in casks. In certain districts it was stored in pits for several months before grinding, whereby its tinctorial power was said to be greatly enhanced; but these and other refinements of its preparation are now of so little importance as to be hardly worthy of mention. The root in many countries bears the name "alizari" or "lizari," whence we have the name "alizarin". Madder was principally cultivated in Holland, France, and Turkey, and to a less extent in Belgium, Italy, and Germany, and North and South America, but the small quantity which enters this country is principally obtained from Holland. Perhaps no substance was submitted to so much examination by the older chemists as madder, and in many of the earlier works on dyeing much space is occupied by a description of these researches.

The isolation of the most important colouring matters of madder, alizarin, and purpurin, occurred as far back as 1826 and 1828, and was due to the chemists Robiquet and Colin; but it is doubtful whether they were successful in obtaining these substances in a state of chemical purity. By many of the earlier workers it was considered that these colouring matters did not exist as such in madder, but were present in combination with sugar or some other substance. About 1823 Kuhlmann extracted a bitter-sweet yellow amorphous compound from the root and named it xanthin, and a similar yellow substance was also isolated by Runge and Watt. In 1848 Higgin observed that if a cold aqueous solution of madder, which has a deep yellow colour and an intensely bitter taste, was allowed to stand for some time or was heated to 50°, it lost these characteristics, and a gelatinous flocculent precipitate was formed in which all the tinctorial power of the original infusion resided. Higgin considered, therefore, that the xanthin of madder must, during this process, have been converted into alizarin, and that the change was probably brought about by the action of some ferment contained in the madder, and extracted along with the xanthin by cold water. Somewhat latter (1851) Schunck isolated from madder a substance which he called rubian, as a dark, brownish-yellow-transparent, amorphous hard mass, which by hydrolysis with acids or by the action of the special madder ferment, which he termed "erythrozym," was converted into glucose, alizarin, and other substances.

The next important step was due to Rochleder, who prepared the alizarin glucoside in a crystalline condition and named it *ruberythric acid*. It appeared to possess the formula $C_{20}H_{22}O_{11}$, and its hydrolysis could be represented according to the following equation :—

$$C_{20}H_{22}O_{11} = H_2O + \underset{\text{Alizarin.}}{C_{14}H_8O_4} + \underset{\text{Sugar.}}{C_6H_{12}O_6}$$

Subsequently, Schunck prepared a crystalline compound, rubianic acid, which he regarded as an oxidation product of rubian, and which proved to be identical with the ruberythric acid of Rochleder.

Finally, this portion of the subject was exhaustively examined by Liebermann and Bergami, who assigned the formula $C_{26}H_{28}O_{14}$ to ruberythric acid, and proved that its hydrolysis with acid proceeds as follows :—

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6$$

For the preparation of the glucoside, madder (1 kilo.) is extracted with boiling absolute alcohol (8—9 litres) for two to four hours, and the mixture filtered hot. The alcoholic extract is evaporated to about one-quarter its bulk, and on cooling a yellowish-brown crystalline precipitate of the impure glucoside separates. After filtering and evaporating the filtrate still further, crystals of cane sugar separate, and by adding water to the remaining alcoholic solution impure alizarin is precipitated. In this way, according to Liebermann and Bergami, 1 kilo. of madder gave

Impure glucoside . .	50—60 grams	(5—6 per cent.)
„ sugar . . .	15—30 „	(1·5—3 „)
„ colouring matter .	30—40 „	(3—4 „)

The impure glucoside, which becomes resinous on drying, is dissolved in water, the solution is precipitated with lead acetate, filtered, and the filtrate treated with basic lead acetate. The pink coloured precipitate is well washed, suspended in water, decomposed with sulphuretted hydrogen, and the lead sulphide, which contains also the liberated ruberythric acid, is collected and washed with cold water. The ruberythric acid is removed from the lead sulphide by means of boiling alcohol, the yellow extract is partially evaporated, water and some quantity of barium hydroxide solution are added, and, after filtering off a white precipitate, an excess of barium hydroxide is added to the filtrate. The dark cherry-red precipitate of barium ruberythrate is dissolved in acetic acid, the solution is filtered, barely neutralised with ammonia, and then treated with

basic lead acetate. The resulting red precipitate is washed with alcohol, suspended in alcohol, and decomposed by hydrogen sulphide, and the liquid and precipitate together are heated to boiling and filtered hot. On cooling, the amber-coloured solution yields pale yellow needles of ruberythric acid which are recrystallised from hot water. The latter portion of this process, employed by Liebermann and Bergami, is due to Rochleder.

Ruberythric acid crystallises in silky needles of a pure yellow colour, melts at 258—260°, and when strongly heated yields a sublimate of alizarin. It dissolves in caustic alkali solutions with a cherry-red colour, which on boiling changes to violet, and on acidification yields a precipitate of alizarin. With potassium carbonate solutions, dark red needles of potassium ruberythrate are produced. Ruberythric acid is not precipitated with lead acetate, but basic lead acetate gives a red flocculent precipitate. It possesses no dyeing power.

By the action of sodium acetate and acetic anhydride, Liebermann and Bergami obtained an *octoacetyl* derivative $C_{26}H_{20}O_6(C_2H_3O_2)_8$, which crystallises in yellow needles, melting at 230°.

Schunck and Marchlewski, by means of the method of Schotten and Baumann, obtained a *hexabenzoyl* and a *heptabenzoyl* compound. The fact that ruberythric acid gives an octoacetyl derivative renders two constitutions possible for this substance, viz. :—

(1) $C_{14}H_6O_2\begin{cases}O \cdot C_6H_7O(OH)_4\\O \cdot C_6H_7O(OH)_4\end{cases}$

(2) $C_{14}H_6O_2\begin{cases}O \cdot C_{12}H_{14}O_3(OH)_7\\OH\end{cases}$

and of these the second is more probably correct, as an explanation is thus afforded of the well-characterised red-coloured salts which can be obtained from it.

Erythrozym, the madder enzyme, was obtained by Schunck by extracting madder with water at a low temperature (38°) and precipitating the solution with alcohol. When dried, it consisted of a brown amorphous mass. Under its influence, ruberythric acid is hydrolysed with formation of alizarin and glucose. This reaction no doubt takes place in the incompletely dried root on storing, and it is evidently due to this fact that madder was said to dye more readily after this treatment. In dyeing with madder, moreover, the presence of this enzyme will no doubt exercise a beneficial effect, because as it is frequently the practice to employ at first a cold dye-bath and then to gradually raise the temperature, hydrolysis of the glucoside,

which is itself devoid of tinctorial property, will thereby occur with formation of the colouring matter.

Though purpurin is considered to exist in madder in the form of glucoside, such a compound has not yet been isolated, and some uncertainty exists on this point. During some experiments carried out by Perkin, it was found that an alcoholic extract of madder, on standing in cold weather, deposited a considerable quantity of cane sugar contaminated with a red precipitate. This latter was soluble in water, and on treating the solution with cold dilute acid, gave a precipitate of impure purpurin and appeared to consist of an acid calcium salt of this substance. On the other hand, it was not ascertained whether all varieties of madder behave similarly in this respect, and the matter requires further investigation. Presuming, however, that a purpurin glucoside is present in madder, it is evident that this compound is far less stable than ruberythric acid, and is hydrolysed by dilute acids at a temperature at which the latter is unaffected.

Kopp's Process for the Extraction of Madder.

Based on this assumption, the commercial process of Kopp was devised, and this is specially interesting as it affords a fairly complete method for the isolation of the phenolic constituents of this dyestuff.

Ground madder is extracted with a cold aqueous solution of sulphurous acid, and the solution, after addition of 2—3 per cent. of hydrochloric acid (33 per cent.), is heated to 60°. A red flocculent precipitate of purpurin is thus thrown down which was collected, washed, dried, and sold under the name of "commercial purpurine" or "Kopp's purpurine". This product was until recently prepared to a very small extent in France for the manufacture of a rose-red lake, and for this purpose gives results differing in some respects from those produced by the artificial dyestuff.

Kopp's purpurine, in fact, is not pure purpurin, but consists mainly of a mixture of this colouring matter with three other substances: *pseudo*-purpurine, purpuroxanthin, and purpuroxanthin carboxylic acid or munjistin.

Pseudo-purpurin was first isolated from Kopp's commercial product by Schützenberger and Schiffert, but the fact that it consists of a purpurin carboxylic acid is due to the investigation of Rosenstiehl. It consists of small red prismatic needles, and differs from purpurin in that it is more readily soluble in benzene. It melts at 218—220° with evolution of carbon dioxide and formation of purpurin, and this decomposition is said to occur gradually at from 180—195°. Purpurin is also produced by boiling *pseudo*-purpurin with dilute caustic alkali,

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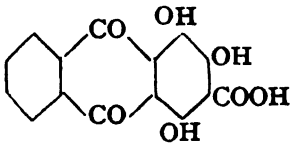
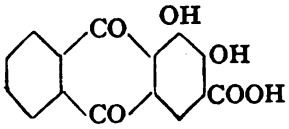
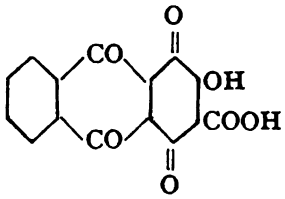
or by long boiling with water or alcohol. The constitution of *pseudo*-purpurin is represented by the following formula:—



It may be prepared synthetically (D.R.P. 260765) by dissolving 1 . 2 dihydroxyanthraquinone 3 carboxylic acid—

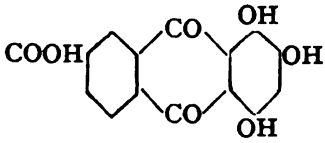


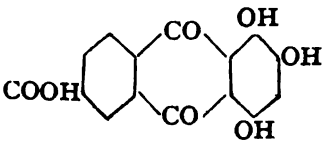
in 20 parts of sulphuric acid and slowly treating the solution at 15—20° with 0·3—0·4 parts of manganese dioxide. In place of the 1 . 2 dihydroxy the 1 . 4 . 3 dihydroxycarboxylic acid may be employed (D.R.P. 272301), in which case the 2 hydroxyanthradiquinone carboxylic acid is the first product of the reaction—



This by means of sodium hydrogen sulphite solution is reduced to *pseudo*-purpurin.

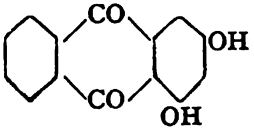
It is interesting to observe that an isomeric compound which is obtained by the oxidation of alizarin carboxylic acid, and for which also the two formulæ—





are possible, differs markedly from *pseudo*-purpurin, and is an exceedingly stable compound (Perkin and Cope).

Purpuroxanthin or xanthopurpurin, which forms glistening yellow needles, melting at 262—263°, is a dihydroxyanthraquinone isomeric with alizarin, and was isolated from Kopp's purpurin by Schützenberger and Schiffert. These authors also found that purpuroxanthin can be produced by digesting purpurin with phosphorus iodide and water, or by the action on it of a boiling alkaline stannous chloride solution. The reverse action occurs, according to Rosenstiehl, when an alkaline solution of purpuroxanthin is boiled with excess of air, purpurin being thus produced. Purpuroxanthin was synthesised by Noah by heating 3 : 5-dihydroxybenzoic acid with benzoic acid in the presence of sulphuric acid, and possesses the following constitution:—



According to Plath, the dimethyl ether melts at 178—180°, and the diacetyl derivative (Liebermann) at 183—184°.

Purpuroxanthin dyes aluminium mordanted fabrics a yellow colour (Schützenberger and Schiffert).

Purpuroxanthin carboxylic acid (munjistin) was discovered by Schunck and Römer in the crude purpurin. It crystallises from acetic acid in golden yellow leaflets, melts at 231°, and dissolves in alkaline solutions and ammonia with a red coloration. By heating above its melting-point or by boiling with alkalis, it is converted into purpuroxanthin. It has not been prepared synthetically, but probably contains its carboxyl group in a similar position to that present in *pseudo*-purpurin. It is said to dye aluminium mordanted fabrics an orange-red colour, which is, however, not fast to the action either of soap or light.

GREEN ALIZARIN.—The sulphurous acid liquid from which the purpurin precipitate has been removed is boiled for two hours, when the ruberythric acid and certain other glucosides present are hydrolysed and a deep green precipitate separates. This at one time was a commercial article, and was known under the name of "green alizarin".

CHLORORUBIN.—The green tinge of this product arises from the presence in madder of a considerable quantity of a peculiar substance, possibly a glucoside, termed chlorogenin or rubichloric acid, but little

or nothing is known of its chemical nature. It is also present in chay root, morinda root, in certain species of *galium* and in the *Gardenia grandiflora*. This compound, which has been obtained in the form of a colourless syrup and to which the formula $C_{14}H_8O_9$ has been assigned, on digestion with boiling dilute mineral acid, is converted into chlororubin and formic acid. Chlororubin consists of a dark green amorphous powder which is insoluble in all the usual solvents, but dissolves in alkaline solutions with a blood-red colour.

YELLOW ALIZARIN.—In order to obtain this product, the dried and finely powdered "green alizarin" was extracted at 150° with petroleum (toluene or coal-tar solvent naphtha is more suitable for laboratory purposes), by which means the alizarin and other phenolic constituents pass into solution, whereas the chlororubin remains undissolved. The petroleum extract after cooling is agitated with 10 per cent. caustic soda solution, and the dark violet-coloured alkaline liquid thus produced is removed and neutralised with acid. The bright yellow precipitate was collected, washed and dried, and sold under the name of "yellow alizarin".

The alizarin prepared in this manner is not completely pure, as it contains a small quantity of a mixture of non-tinctorial substances, which are derivatives of anthraquinone. To remove these, an alkaline solution of the "yellow alizarin" is treated with milk of lime, which precipitates the alizarin in the form of its calcium compound. This when collected, well washed, and decomposed with acid, gives a very pure alizarin which is best crystallised from solvent naphtha.

If the reddish-brown filtrate from the calcium alizarate is neutralised with acid, a small quantity of a dull yellow precipitate separates which is approximately equal to 0·02 per cent. of the madder employed. A preliminary examination of this product indicated that it consisted of at least four yellow crystalline substances, with no special properties that would permit of their ready separation.

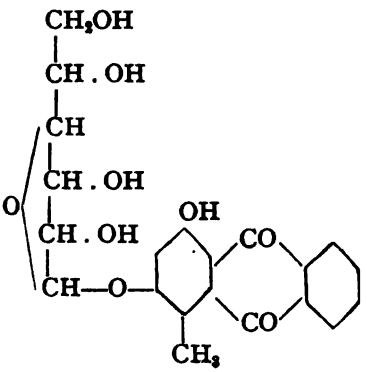
Schunck during his examination of madder obtained various yellow crystalline and amorphous products by the action of acids and alkalis on his rubian. The individuality of most of these substances, to which the names rubiretin, verantin, rubiadin, rubianin, rubiafin, rubiagin, rubiadipin, rubidehydran, rubihydran, and rubiacic acid were assigned, has been doubted by later writers, and but one of these—namely, rubiadin—has been characterised. On the other hand, it is quite possible that certain of these may exist in the mixture of yellow non-tinctorial substances previously referred to. For a description of his compounds, the original papers of Schunck should be referred to.

Rubiadin glucoside (Schunck and Marchlewski).—Madder is extracted with boiling water, the solution precipitated with lead acetate, and the filtrate treated with ammonia, by which means a second lead precipitate is formed. The latter is decomposed with sulphuric acid, the lead sulphate removed, and the clear liquid boiled with addition of hydrochloric acid. A dark green precipitate separates, only a portion of which dissolves in boiling alcohol. On treating the alcoholic extract with lead acetate, the alizarin present can be removed, and addition of baryta water now precipitates the barium salt of the rubiadin glucoside, which is decomposed by dilute hydrochloric acid. It crystallises from alcohol in citron yellow needles, melts at 270° with decomposition, and when hydrolysed by acid gives rubiadin and glucose—

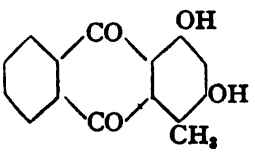
$$C_{13}H_{20}O_9 + H_2O = C_{15}H_{10}O_4 + C_6H_{12}O_6$$

Penta-acetylrubiadin glucoside, yellow needles, melts at 237°.

According to Marchlewski, the constitution of this glucoside is best expressed as follows:—



Rubiadin, prepared by the hydrolysis of the glucoside, forms yellow needles, melting about 290°, soluble in alkalis with a red coloration. By oxidation with chromic acid it gives phthalic acid. Rubiadin, according to Schunck and Marchlewski, is a methyl purpuroxanthin and possesses the following constitution:—



Rubiacin (Runge's madder orange) is a yellow crystalline substance obtained directly from the madder root, and is formed, according

to Schunck, by the decomposition of a glucoside. It separates in small quantity from an infusion of madder made with only a little cold water, after it has become sour by twelve hours' standing. It crystallises in the form of plates and needles, having a strong reddish-green lustre. Alkalis dissolve it with a purple colour.

The following table illustrates the analysis of madder by the sulphurous acid extraction method :—

Madder is extracted with dilute sulphurous acid solution and the extract heated to 60°.

Precipitate consists of Purpurin, Pseudo-purpurin, Purpuroxanthin carboxylic acid, Purpuroxanthin.	Filtrate is digested with boiling dilute H_2SO_4, and the resulting precipitate of green alizarin extracted with boiling toluene or petroleum.
Chlororubin remains undissolved.	The toluene extract is agitated with caustic soda solution, and the alkaline liquid is treated with baryta water.
Precipitate consists of calcium alizarate, which when decomposed with acid gives alizarin.	Filtrate on acidification gives a precipitate of yellow non-tinctorial derivatives of anthraquinone.

Commercial Preparations of Madder.

The principal of these were: Garancine, Garanceux, Flowers of Madder, Commercial Alizarin or Pincoffin, and Madder extract.

Garancine.—The preparation of this product results from the observation in 1827 of Robiquet and Colin, that by treating ground madder with an equal weight of concentrated sulphuric acid, the various principles of the madder were destroyed with the exception of the colouring matter alizarin. We now know further that the glucoside of the root is decomposed by the action of the acid. This first product was termed *charbon sulphurique*, but soon the method of its preparation was slightly altered, and it then received the name *garancine*.

Garancine is made by mixing, in a wooden tank with false

bottom, 100 kilos. ground madder, 1000 litres water, and 2 kilos. sulphuric acid, 168° Tw. (sp. gr. 1·84), stirring up and allowing the whole to macerate for about twelve hours. The liquid is then drawn off, the residue mixed with a little water and 30 kilos. strong sulphuric acid, and the whole boiled for 2—3 hours. After running off the acid liquor, the garancine remaining is washed with water till free from acid, drained, pressed, dried, and ground.

The colouring power of garancine is three to four times that of good madder, it dyes more readily, giving yellower toned reds and pinks, and greyer lilacs. They are not quite so fast to soap as the madder colours, but since, in the case of printed calicoes, the unmordanted white parts are not so much soiled in the dye-bath, the operation of soaping can be omitted.

Garanceux or *Spent Garancine* was introduced in 1843 by L. Schwarz of Mulhouse. It was simply a low quality of garancine prepared in the above manner from the spent madder of the dye-baths, and made by each calico-printer for himself, by way of economy. Its colouring power is about one-fourth that of good garancine.

Flowers of Madder was first made in 1851 by Julian and Rogner of Sorgues. It can be prepared by macerating ground madder for several hours with cold water very slightly acidulated with sulphuric acid (1—2 per cent. on the weight of madder), then washing, draining, pressing, drying, and grinding. In this manner all soluble, mucilaginous, and sugary matter, etc., is removed, decomposition of the glucoside by fermentation occurs, and the residue has nearly double the colouring power of the original madder. The waste liquors were neutralised, allowed to ferment with the addition of yeast, and then distilled to gain the alcohol. 100 kilos. madder yielded 45—60 kilos. flowers of madder and 10 litres alcohol, suitable for making varnish, etc.

Commercial Alizarin or *Pincoffin* was introduced in 1852 by Schunck and Pincoff, who prepared it by submitting ordinary garancine to the action of high pressure and superheated (150° C.) steam. By this treatment the vèrantin and rubiretin present in the garancine were said to be destroyed, while the alizarin remained intact, and the product yielded in consequence more brilliant purples, and less soaping was required to clear the whites or unmordanted portions of printed calicoes.

Madder Extracts.—Already in 1826 attempts were made by Gaudin to apply mordants along with the colouring matter of madder directly to calico, in the form of an extract, i.e. as a steam-

colour, instead of by dyeing, and in 1837 Gastard succeeded in doing this successfully on a large scale by means of a product named *colorine*. The expense, however, of this and other early madder extracts retarded their application, but their utility having been clearly demonstrated, the endeavours of numerous chemists were directed to their production in a reasonably cheap manner. Madder extracts consisted of variable mixtures of the two colouring matters of madder, alizarin and purpurin, or of each separately, in a more or less pure condition. By the introduction of artificial alizarin, just when their manufacture had been perfected, they lost all their importance. The following were the chief methods of production employed.

Leitenberger's process consisted in first extracting all the purpurin from ground madder by water heated to 55° C., and afterwards dissolving out the less soluble alizarin from the dried residual madder by means of wood-spirit. The aqueous solution was precipitated by lime, the washed calcium-purpurin lake was then decomposed with hydrochloric acid, the liberated purpurin collected and washed, when it was ready for use. The alcoholic solution of alizarin was merely precipitated by water, collected and washed. Alizarin and purpurin extracts were thus obtained.

Paraf's method (1868) consisted in extracting madder with superheated water, with or without the addition of a small quantity of alum or sulphuric acid, then collecting and washing the flocculent alizarin precipitate which separated out on cooling.

The modes of preparing Kopp's "purpurine," "green alizarine," and "yellow alizarine" have already been given.

Pernod's madder-extract, once largely used, was prepared by extracting garancine with boiling water very slightly acidified with sulphuric acid, collecting and washing the precipitate thrown down on cooling, and extracting the dried precipitate with boiling alcohol. After recovering the major portion of the alcohol by distillation, the remaining solution was mixed with water, and the precipitated alizarin was collected and washed.

Use of Madder in Dyeing.

Previous to 1870 madder and its derivative garancine were the dyestuffs *par excellence* of the calico-printer and Turkey-red dyer.

By the former, it was used because of its characteristic property of yielding a variety of colours with the aluminium, tin, and iron mordants, viz. red and pink, orange, lilac, and black; also brown or chocolate, by employing a mixture of aluminium and iron mordants. Further, all these colours are fast to soap and light. To the calico-

printer both the alizarin and the purpurin of the madder were of use, though undoubtedly the alizarin would, in most styles of work, be the essential colouring matter. The Turkey-red dyer employed madder, and afterwards garancine, because they yielded, by his peculiar process, the most brilliant and most permanent red on cotton which was known. In this case the alizarin was the all-important colouring matter, since the purpurin, although fixed on the fibre at first, was more or less removed during the operations of clearing. Alizarin, in conjunction with aluminium and iron mordants, gives a bluish-red and a comparatively bright lilac; purpurin, a yellowish-red and a greyish-lilac, respectively.

The method of applying madder in Turkey-red dyeing was similar to that now employed in the case of alizarin.

Another interesting feature in connection with the application of this dyestuff is that, if the madder was deficient in lime, it was necessary to add a certain proportion of chalk to the dye-bath; it now appears that calcium is a normal constituent of the madder colours, especially those obtained with aluminium and iron mordants.

Madder has also been used in the past, and is even now employed to a small extent, by the indigo dyer and the woollen dyer.

Literature.—Robiquet and Colin, Ann. Chim. Phys., [ii.], 34, 225; Robiquet, *ibid.*, 63, 311; Annalen, 20, 196; Kuhlmann, J. Pharm. Chim., 14, 354; Zenneck, Pogg. Ann., 13, 261; Decaisne, J. Pharm. Chim., 24, 424; Gaulthier de Claubry and Persoz, Annalen, 2, 31; Runge, J. pr. Chem., [i.], 5, 362, 374; Higgin, Phil. Mag., [iii.], 33, 282; J. pr. Chem., [i.], 46, 1; Schützenberger, Bull. Soc. Chim., [ii.], 4, 12; Schunck, Phil. Trans., 141, 433; 142, 67; 145, 389; Annalen, 66, 174; 81, 151, 344; 87, 345, 351; Schunck and Römer, Ber., 10, 172, 551, 790; Debus, Annalen, 66, 351; Wolff and Strecker, *ibid.*, 75, 3; K. Moy, *ibid.*, 54, 346; H. Koechlin, *ibid.*, 59, 344; Schiel, *ibid.*, 60, 79; De Lalande, J., 1874, 486; E. Kopp, Bull. Soc. Ind. Mulh., 1861, 31, 9; 1867, 37, 437; Rochleder, Annalen, 80, 323; 82, 207; Schwarz, *ibid.*, 80, 333; Willigk, *ibid.*, 82, 339; Stenhouse, *ibid.*, 130, 341, 343; Bolley and Rosa, Dingl. poly. Jahr., 171, 446; Strecker, J., 1868, 479; Rosenstiehl, Ber., 7, 1546, 10, 1178; Liebermann and Bergami, Ber., 25, 2241; Liebermann and Plath, Ber., 10, 1618; Liebermann and Friedländer, Ber., 29, 2851; Schunck and Marchlewski, Chem. Soc. Trans., 63, 969, 1137; 65, 182; Gmelin, Handb., 16, 32; 14, 129; Perkin and Cope, Chem. Soc. Trans., 65, 848.

Chay Root.

Chay Root or Chay-aver (from chaya = which fixes colours, and ver = root), also called Indian madder, is the root of *Oldenlandia umbellata* (Linn.), Rubiaceæ. It bears the following Indian vernacular names: turbuli (Bengali); cheri-vello (Telugu), ché or chay, sayawer, imburel (Tamil). The plant is a small bush or herb found on sandy soils, chiefly near the sea-coast. It occurs in North Burma and Ceylon, but is most abundant in certain tracts of the Madras Presidency, from Orissa southward. It does not appear to be used in Bengal, but on the Malabar and Coromandel coasts, especially the latter, it is or was extensively cultivated, and employed in dyeing a colour analogous to Turkey-red. The chief market is Madras, where it was sold in small bundles at about 4d. a lb. The roots are usually about 10—12 inches long and ¼ inch thick, somewhat straight and stiff, tough and wiry, and with few or no lateral fibres. When freshly gathered, they have an orange colour; but when dried and kept, they assume a yellowish-grey hue. Boiling water gives merely a pale yellow extract, but if alkali is added, a blood-red decoction is soon obtained. The colouring principles seem to reside chiefly, if not entirely, in the bark of the root.

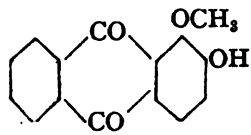
The older literature connected with chay root is extremely meagre, and is for the most part contained in the following publications: "Philosophy of Permanent Colours," 2282, 1813, Bancroft; "Bulletin de la Société industrielle de Mulhouse," 5302, 1832, E. Schwartz and D. Koechlin; "L'Art de la Teinture des Laines," 475, 1849, Gonfreville. Quantities of the root were imported into Europe in 1774 and at later periods, and its dyeing properties were examined by the above-mentioned experts. It met with little practical application, however, as it was not found to possess any advantage over madder; indeed, it was considered to have but one-half or even a fourth of the colouring power of madder; further, it was found to contain certain undefined yellow substances of an acid character, which interfered somewhat with its dyeing power. Still, it was recognised as a good dyestuff, giving the usual madder colours, and equally fast to soap. It is evident that the yellow substances referred to are not the same as those described in this chapter, as Schwartz states that they were present in larger quantity in "nona" (*Morinda citrifolia*) than in chay root, whereas the yellow substances described later exist in much larger quantity in chay root than in morinda root. Very probably they refer to Rochleder's "rubichloric acid," as this is contained in morinda root in larger amount than in chay root. Schützenberger, in his

"Traité des matières colorantes," 2, 291, 1867, states that he found chay root to contain alizarin and chlorogenin (rubichloric acid) and that it was easy to exhaust the root by extraction with alcohol.

In many respects chay root resembles madder, as both contain ruberythric acid, alizarin, rubichloric acid, and cane sugar, but there are very marked differences in the nature of the other constituents of the two roots. Madder, as is well known, contains purpurin, purpurin- and purpuroxanthin-carboxylic acids, etc., and but traces of yellow crystalline substances, forming barium compounds soluble in water, which have not been fully investigated. In chay root the former substances are entirely absent, but, on the other hand, although the root contains considerable quantities of yellow crystalline substances, they are quite distinct from those contained in madder.

The phenolic constituents of this root have been studied by means of the sulphurous acid extraction method described in detail in connection with madder, and also by a subsequent exhaustion of the residual root with boiling lime-water. In this manner, chlororubine, alizarin, and a mixture of non-tinctorial yellow substances were isolated. These latter are present in chay root (probably as glucoside) in comparatively large amount (1 per cent.) and have been shown to consist principally, if not entirely, of the following substances.

Alizarin α-methylether crystallises from dilute methyl alcohol in long orange-yellow needles, melting at 178—179°. It has the constitution—



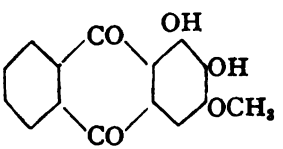
This compound may be synthesised by the action of an ethereal solution of diazomethane on a nitrobenzene solution of monoacetyl alizarin (Oesch and Perkin, Proc. Chem. Soc., 1914, 30), subsequently removing the acetyl group. Owing to the fact that the so-called monoacetyl alizarin is a mixture of the two monoacetyl alizarins, both α and β-alizarin methylethers are thus simultaneously produced. Addition of alcoholic potash to a solution of the product in alcohol causes the precipitation of the β-methylether as potassium salt, the α-methylether thus remaining in solution.

The methoxyl group present in this substance is much more readily hydrolysed than is usually the case, for prolonged digestion with boiling baryta water is sufficient for this purpose, a precipitate consisting of barium alizarate thus separating. This property, there-

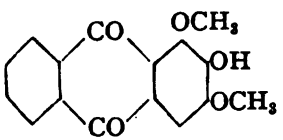
fore, accounts for the difficulty in obtaining either this compound or alizarin dimethylether by means of methyl iodide, for in this process of methylation a prolonged digestion in the presence of free alkali is necessary. On the other hand, whereas alizarin is only converted with considerable difficulty into alizarin dimethylether, by the action of methyl sulphate, alizarin α-methylether readily yields this substance when treated with this reagent in the usual manner.

Acetylalizarin α-methylether crystallises in yellow needles, melting at 212°.

Anthragallol dimethylether (A) forms yellow needles, and dissolves in alkaline solutions with a red coloration. It is distinguished from the isomeric compound described below, in that it yields an ammonium salt, crystallising in scarlet prisms, which is sparingly soluble in cold alcohol. Heated with sulphuric acid to 180°, or with hydrochloric acid, it is converted into anthragallol, and when methylated by means of methyl sulphate, is readily converted into anthragallol trimethylether. By the action of 10 per cent. potassium hydroxide in a sealed tube at 180° for five hours, it is partially converted into methoxyalizarin—

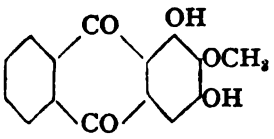


and a similar reaction occurs when sulphuric acid at 100° is employed. The constitution assigned to this anthragallol dimethylether (A) is therefore as follows :—

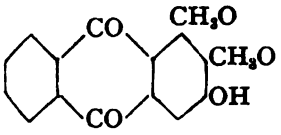


Acetylanthragallol dimethylether crystallises in pale yellow prisms, melting at 213—215°.

Anthragallol dimethylether (B) crystallises in yellow leaflets, melting at 230—232°, and gives a red ammonium salt which is soluble in cold alcohol. Heated with 10 per cent. potassium hydroxide solution to 180° for five hours, it is partially converted into a compound having the reactions of methoxypurpuroxanthin—



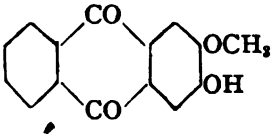
and most probably possesses the following constitution :—



By methylation with methyl sulphate in the usual manner, this compound is readily converted into anthragallol trimethylether.

Acetylanthragallol dimethylether (B) consists of long yellow needles, melting at 176—178°.

Hystazarine monomethylether obtained as long orange-yellow needles, melting at 232°, when heated with hydrochloric acid at 180°, is converted into hystazarine. Alkaline solutions dissolve it with a crimson coloration, and its ammonium and potassium salts, which crystallise in garnet-red needles, are insoluble in cold *iso*-butylic alcohol. The constitution of hystazarine monomethylether is as follows :—



By means of methyl sulphate, it yields hystazarine dimethylether, which consists of yellow glistening needles, melting at 235—236°.

Metahydroxyanthraquinone, pale yellow needles, melting at 302°, is identical with the well-known artificial compound prepared from anthraquinone-β-monosulphonic acid by digestion with alkali.

Dyeing Properties.—Although chay root contains acid principles which tend to dissolve the mordants, its employment as a dyestuff presents no difficulty. The only precautions necessary to be observed are to add 2 per cent. of chalk to the dye-bath, and to raise the temperature gradually to the boiling-point.

Dyeing experiments on ordinary stripe-printed calico, containing alumina and iron mordants, have shown that the dyeing power of chay root is equivalent to the presence of a percentage of 0·33—0·35 alizarin. Compared with ground madder root of good quality, it seems to have about half its dyeing power when the comparison is

made before soaping, but after soaping it appears to be quite equal to madder. The reds, pinks, and chocolates have a distinctly bluer shade than those given by madder, and the lilacs are much fuller and brighter and very similar to those obtained from alizarin. This last feature alone ought to have secured a ready market for chay root among the European dyers, previous to the introduction of artificial alizarin, and it is somewhat strange that its marked suitability for lilacs should have escaped the observation of those who formerly made dyeing experiments with this root.

On oil-prepared calico, mordanted with alumina, chay root gives an excellent blue shade of Turkey-red, withstanding the operation of clearing with soap and stannous chloride better even than a madder-dyed red, and quite equal to one obtained by means of artificial alizarin. Good brown, red, orange, and purple colours are readily obtained on wool, and also on silk, suitably mordanted with chromium, aluminium, tin, and iron, according to the ordinary method usual with dyers. On wool, the colours not being submitted to any soaping operation, chay root appears to possess about half the dyeing power of madder.

Boiled with dilute sulphuric acid, chay root yields a "garancine" of a very dark green colour and possessing about three times the dyeing power of the original root.

Literature.—A. G. Perkin and J. J. Hummel, Chem. Soc. Trans., 1893, 63, 1160; *ibid.*, 1895, 817; A. G. Perkin, *ibid.*, 1907, 91, 2066; J. J. Hummel and A. G. Perkin, J. Soc. Chem. Ind., 1894, 13, 346.

GALIUM.

The roots of various species of galium have been employed to some extent for dyeing red on aluminium mordant, and Bancroft in his "Philosophy of Permanent Colours" (vol. ii., 303) mentions six of these plants, the roots of which gave an excellent red in this manner. More especially he refers to the *Galium tinctorium*, the roots of which, about 2 feet in length, are of a dark reddish colour, and which were employed by the French inhabitants of Canada to dye their cloths red.

This product is also referred to by Hellot, p. 161, as a species of madder brought from Canada which possesses an extremely slender root and produces nearly the same effect as European madder.

According also to Bancroft the roots of the nearly allied species of *Asperula*, of which he specially mentions the *Asperula tinctoria*

known as "Dyer's woodruff," were at one time used for dyeing red instead of madder (p. 307).

Of others may be mentioned the *Galium mullugo*, Great Ladies' bedstraw or Wild madder, *Galium verum*, Yellow Ladies' bedstraw, and *Galium aparine*, the well-known Cleaver's or Goose grass, the two latter of which are common to this country. The roots of this last certainly give a small amount of dye soluble in alkali with a purple colour, and there seems to be little doubt that all contain dyes which are fast to light and of the alizarin type, though they appear to give a somewhat yellower shade than alizarin itself. An examination of these in case they yield either anthrapurpurin or flavopurpurin would be interesting.

Munjeet or Manjeet.

The *Rubia cordifolia* (Linn.) was formerly extensively cultivated in India, particularly in the mountainous districts, for the sake of the colouring matters contained in its stem or roots. In the Darjeeling district it occurs as a small climber common all over the hills, at elevations varying from 3000 to 7000 feet, but most abundant between 5000 and 6000 feet, and is found either creeping along the ground or climbing the trunks of trees in large festoons. In Bengal it would seem that the dye of munjeet is extracted mainly from the stem, and only occasionally from the root, as is the case in the North-Western Provinces and elsewhere in India. The munjeet of Bengal is apparently rather the *Rubia munjista* of Roxburgh than the *Rubia cordifolia*. This species of Roxburgh is, however, reduced to *Rubia cordifolia* in Hooker's "Flora of British India". To prepare the dye the wood of the munjeet is first dried, then crushed and pounded, and then generally boiled with water, but sometimes merely left to steep in cold water. The solution obtained is of a deep red, and is used generally to dye coarse cotton fabrics, or the thread which is to be woven into such fabrics. Alum appears to be generally employed as a mordant, although myrobalans also are used in the Darjeeling district, and other astringents in the Maldah district. In the latter district munjeet is used in conjunction with iron salts to produce a deep purple, and in the Darjeeling district is mixed with indigo to form a maroon (McCann, "Dyes and Tans of Bengal"). The red and chocolates of East Indian chintzes were formerly entirely obtained from munjeet. The colours produced from munjeet are bright, but not so durable as those from ordinary madder, the inferiority being due, according to Stenhouse (Pharm.

Jahr., 13, 148), to the presence of purpurin and an orange dye munjistin (purpuroxanthin carboxylic acid). Runge, who examined the tinctorial power of munjeet, concluded that it contained twice as much available colouring matter as madder; but later experiments have shown that the colouring power is actually less. Stenhouse found that munjeet garancine has only half the colouring power of garancine made from Naples roots, but that munjeet yields (according to Higgin) from 52—55 per cent. of garancine, whereas madder yields only 30—33 per cent.

When madder was so much in vogue, munjeet was employed to some extent in this country, because it was considered that a good quality of this material contained as much colouring matter as madder, and could be applied by exactly the same methods.

The important colouring matter of munjeet is *purpurin*, and no alizarin is present in this root, and it is therefore interesting to note that whereas chay root contains alizarin, and munjeet purpurin, in madder both these substances exist together.

For the analysis of the phenolic constituents of munjeet, a modification of the method of Stenhouse, who first submitted this plant to examination, is to be recommended.

The ground dyestuff is digested with boiling alum solution for five hours, and the deep red extract treated with acid and allowed to cool. The red precipitate is collected, washed, and dried, and then extracted with boiling toluene (carbon disulphide was employed by Stenhouse), by which means the colouring matters pass into solution, and a resinous impurity remains undissolved. The colouring matters are now removed from the toluene by agitation with dilute potassium hydroxide solution, the alkaline liquid is acidified, and the precipitate collected, washed, and dried. In order to separate the constituents of this product it is extracted about ten times with boiling dilute acetic acid, and the dark red residue consisting of *purpurin* is crystallised from alcohol.

The earlier acetic acid extracts are mixed with hydrochloric acid, and the yellowish-red deposits are crystallised from alcohol. The product consists of orange-coloured leaflets, and is *purpuroxanthin carboxylic acid* or *munjistin*, as it was termed by Stenhouse, its discoverer, who first obtained it from munjeet. The properties of this compound have already been given in detail under Madder.

Munjeet has also been examined by Perkin and Hummel, who, in addition to the above constituents, detected the presence of a trace of *purpuroxanthin* (Chem. Soc. Trans., 1893, 63, 115).

RUBIA KHASIANA.

According to Watt ("Dictionary of the Economic Products of India," vol. vi., 571) there exists a variety of the *Rubia cordifolia* (Linn.) to which he has assigned the name of *Rubia khasiana*. This form, according also to Watt, is the richest in madder dye principles. It is occasionally met with in Sikkim, but attains its greatest development eastward in the Khásia and Naga Hills. It seems nowhere to be met with to the west of Sikkim. This dyestuff, according to Perkin and Hummel, yields colours similar to those given by *Rubia cordifolia* and *Rubia sikkimensis* (Kurz.), but it possesses a somewhat greater colouring power than either (J. Soc. Chem. Ind., 1894, 13, 348).

RUBIA SIKKIMENSIS (Kurz.).

This Indian dyestuff is closely allied botanically to *Rubia cordifolia* (Linn.); the dried root, which has a rough fluted appearance, is covered with a thick powdery layer of a grey pith-like substance, and looks altogether different from the round, smooth, straight roots of *Rubia cordifolia*. It occurs along with the allied species above mentioned in Sikkim and eastward to the Khásia and Naga Hills, where it is perhaps the most common as it is certainly the largest and most handsome species. Although the root has long been collected and sold in the bazaars at Darjeeling, the plant was not named or even known to exist prior to 1874, having escaped the attention of botanists, who appear to have mistaken it for *Rubia cordifolia*. The Lepchas of Sikkim do not appear to know that *Rubia sikkimensis* yields the madder dye, but in the Naga Hills and in Manipur this species alone supplied the brilliant red dye used by the hill tribes (see "Dyes and Tans of India," 154; Special Catalogue of Exhibits by the Government of India, Colonial and Indian Exhibition, 1886).

The examination of this root, by an identical process to that detailed in connection with Munjeet (*Rubia cordifolia*), has indicated that the phenolic constituents are *purpurin*, *munjistin*, and *purpuroxanthin*. A trace of a red colouring matter approximating to $C_{15}H_8O_6$ in formula was also isolated, but the individuality of this compound has not been definitely established.

Dyeing Properties.—The application of *Rubia sikkimensis* root in dyeing presents no difficulty.

Calico printed with iron and alumina mordants may be dyed without any addition of calcium carbonate or acetate to the bath

since there is a sufficiency of lime naturally present in the root. Generally speaking, the colours with the different mordants are similar to those obtained from madder, but the reds and chocolates are much bluer, being devoid of yellow, and the lilacs are decidedly greyer. The colours, however, are very similar to those obtained from *Rubia cordifolia*, the latter possessing nearly a half more dyeing power.

Comparing the colours on ordinary stripe mordanted calico given by pure purpurin and *Rubia sikkimensis*, a very marked difference is noticeable; the former gives very yellowish-reds and chocolates, full pinks and purplish lilacs, while the latter yields very bluish-reds and chocolates, bare pinks and greyish lilacs.

The dyeing power of *Rubia sikkimensis* is equivalent to its containing 0·37—0·5 per cent. purpurin (Perkin and Hummel, Chem. Soc. Trans., 1883, 63, 1157).

MORINDA CITRIFOLIA.

The roots of *Morinda citrifolia* (Linn.) and *Morinda tinctoria* (Roxb.), known as "Morinda Root," are extensively employed in various parts of India under the general trade name of *Suranji*, more especially for dyeing reds, purples, and chocolates. These plants, the native names for which are *Aal*, *A'l*, *Ach*, or *Aich*, are to be met with in nearly all the provinces of India, either wild as in the jungles of Bengal, or cultivated in small patches in betelnut plantations, or near the homesteads of the dyers. In Bengal the plant is usually propagated by slips or cuttings, but in other parts it is raised from seed, as well as from cuttings. When the plants have attained a height of from 5—6 feet, that is, as a rule, about the end of the third year, the straight spindle-shaped roots which extend into the ground to the depth of 3 or 4 feet, are dug out and the upper portions of the plant are cut into slips to serve for the propagation of the next crop.

The colouring matter is found principally in the root bark, and is developed in greatest quantity at about the end of three or four years, depending upon the character of the soil. After this time the dyeing principle gradually disappears, and the matured trees, which eventually attain the height of a mango tree, contain hardly a trace of it. The thin roots are most valuable, roots thicker than half an inch being thrown away as worthless. They are or were mainly used for dyeing the thread or yarn from which the coloured borders of the cotton garments worn by the lower classes are woven, but they are also employed for dyeing the coarse cotton fabric called "Khárva," or for dyeing the silk thread which forms the border of the silk fabric known

as "Endi cloth". The colours given by A'l range from a reddish-yellow through pink and various shades of red to a dark brown-red. The tint seems to depend primarily upon the age of the root, and upon the proportion of root bark to stem which is employed. The root bark gives the best reds; the dye in the woody part of the root is yellow, and hence when the wood preponderates over the bark the resulting dye is reddish-yellow.

About 1790 some of the powdered root under the name of "aurtch" came into the hands of Dr. Bancroft, who found little or no difficulty in applying it to both wool and cotton. At that time he considered that it might be profitably imported into Europe.

In 1832 Schwartz and Koechlin also examined the root under the names "Nona" and "Hachrout," and reported on its dyeing properties to the Industrial Society of Mulhouse. They referred to the fact that of all the Indian *rubiaceæ* examined by them, it contained the largest quantity of certain yellow principles of an acid character which not only necessitated the washing of the root with cold water before dyeing, but also made it requisite to add a certain proportion of sodium carbonate to the dye-bath in order to have a perfectly neutral bath. Their conclusion was that since morinda root only possessed one-third the dyeing power of a medium quality of madder, it could never compete with the latter in the European market.

About 1848 some morinda root was submitted for trial to some of the most experienced and skilful calico printers of the Glasgow district, all of whom concurred in declaring it not to be a dye at all.

In 1848 Anderson (Annalen, 71, 216) isolated from the root of the *Morinda citrifolia* by extraction with alcohol, a crystalline yellow substance which he named *Morindin*, and to which he assigned the formula $C_{28}H_{30}O_{15}$. This substance when strongly heated, gave a crystalline sublimate *morindon*, and Anderson pointed out the great similarity, on the one hand, between morindin and ruberythric acid, and on the other between morindon and alizarin.

Rochleder (Annalen, 1852, 82, 205) gave it as his opinion that morindin and morindon were identical with the ruberythric acid and alizarin derived from madder, and Stokes (Chem. Soc. Trans., 2, [2], 333) by examining the absorption spectra of solutions of alizarin and morindon in sodium carbonate and in ether, came also to the conclusion that these two colouring matters consisted of one and the same substance. Stenhouse (J., 1864, 17, 543) formed a similar opinion, and pointed out that morindin not only gives morindon by heating, but also when digested with boiling dilute mineral acids.

On the other hand, Stein (J., 1866, 19, 645) found that the

absorption spectra of alizarin and morindon are not identical, and that ruberythric acid and morindin are distinct substances, although the latter resemble each other in the respect that both are glucosides. The distinction between these compounds was rendered much clearer by the work of Thorpe and Greenall (Chem. Soc. Trans., 1887, 51, 52), and Thorpe and Smith (*ibid.*, 1888, 53, 171), who showed that morindon possesses the formula $C_{15}H_{10}O_5$; on distillation with zinc-dust it gave methylanthracene (melting-point 190—191°), and was evidently a derivative of methylanthraquinone. To morindin, the glucoside, the formula $C_{26}H_{28}O_{14}$ was assigned.

Somewhat later Perkin and Hummel (Chem. Soc. Trans., 65, 851), during an examination of the *Morinda umbellata* (Linn.) (*v. infra*), proved that morindon contains three hydroxyl groups, and that Thorpe and Smith's hydrocarbon was β-methylanthracene.

Oesterle and Tisza (Arch. Pharm., 1907, 245, 534) consider that the true formula of morindin is $C_{27}H_{30}O_{15}$, and that its hydrolysis with acid can be expressed as follows:—

$$C_{27}H_{30}O_{15} + 2H_2O = 2C_6H_{12}O_6 + C_{15}H_{10}O_5$$

The sugar thus formed is not fermented by yeast and yields an osazone melting at 197°.*

Morindin crystallises from 70 per cent. alcohol in glistening yellow needles, which melt at 245°, and dissolve in alkaline solutions with a red colour. It does not dye mordanted fabrics.

Nono-acetylmorindin, $C_{27}H_{21}O_{15}(COCH_3)_9$ (O. and T.), citron-yellow needles, melts at 236°?

Nono-benzoylmorindin, $C_{27}H_{21}O_{15}(CO \cdot C_6H_5)_9$ (O. and T.), yellow needles, melts at 186°.

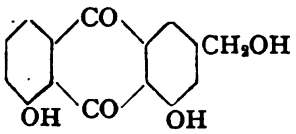
Morindon, the colouring matter of *Morinda citrifolia*, which is obtained by the hydrolysis of morindin, and also exists as a rule to some extent in the free state in this root, consists of orange-red needles, melting at 271—272°. It is soluble in alkaline liquids, with a blue-violet tint, somewhat bluer than the corresponding alizarin solutions, which, when treated with baryta water, give a cobalt-blue precipitate of the barium derivative. Its solution in sulphuric acid is blue-violet.

Triacetylmorindon, $C_{15}H_7O_5(COCH_3)_3$, crystallises in citron-yellow needles, melting at 242°.

Morindon trimethylether, $C_{15}H_7O_2(OCH_3)_3$, is a yellow crystalline powder, melting at 229°.

* Simonsen (private communication in 1918) considers this to be incorrect, and that the formula $C_{26}H_{28}O_{14}$ of Thorpe, Greenall and Smith (cf. Perkin, Chem. Soc. Proc., 1908, 24, 149) correctly represents morindon. See also *M. umbellata*.

The exact constitution of morindon has not yet been determined, but it appears probable that if this compound contains in reality three phenolic hydroxyls, it most likely consists of a methyl anthragallol. If, on the other hand, as is quite probable, morindon contains an alcoholic group, which, according to Robinson and Simonsen, occurs in the isomeric aloe-emodin—



then its constitution will be represented as alizarin in which one of the three β-positions is occupied by CH_2OH. Though such a constitution would appear to harmonise well with the present known properties of morindon, according to Simonsen (private communication) experimental evidence of a CH_2OH group in this compound is lacking.

In many respects the *Morinda citrofolia* resembles chay root and madder, for, in addition to morindin and morindon, it contains a large quantity of *chlorogenin*, and certain yellow non-tinctorial substances, derivatives of anthraquinone. The preparation of morindon in quantity can be conveniently carried out by extraction with sulphurous acid, according to the details given in the sections on Madder and Chay Root for the isolation of natural alizarin. The non-tinctorial yellow compounds, which are obtained as by-products by this method, have not yet been studied in the case of the *Morinda citrofolia*, but in the case of the *Morinda umbellata* have been partially investigated (see below).

From the alcoholic extract of the *Morinda citrifolia*, Oesterle (Arch. Pharm., 1907, 245, 287) has isolated a small quantity of a substance which has the constitution of a *monomethyl ether* of a *trihydroxymethylanthraquinone*. It consists of yellow crystals, melting at 216°, soluble in hot alkaline solutions, with a yellowish-red colour. It is not, as this author suggested, identical with the emodin methyl ether which exists in the *Ventilago madraspatana* (A. G. Perkin, Chem. Soc. Trans., 1907, 2074).

Dyeing Properties.—In Dr. G. Watts' "Dictionary of the Economic Products of India," Dr. J. Murray has written under the head of *Morinda*, not only a most complete account of the more important species, but full details of the native methods of dyeing with them. These methods of dyeing vary considerably in different parts of

India, but they are all similar in general principles, and are practically crude processes of the turkey-red dyeing known in Europe. An extended series of dyeing experiments in connection with morinda root have been carried out by Hummel and Perkin (J. Soc. Chem. Ind., 1894, 13, 346), who find that by adopting certain precautions this dyestuff possesses a dyeing power which is greater than madder itself.

To obtain good results it is necessary, as previously indicated by the work of Schwartz and Koechlin (*loc. cit.*), to neutralise, or better still to remove, the free acid which exists in considerable quantity in the roots. Experiments also with the powdered morinda root which had been allowed to ferment, or had been digested with boiling dilute acid, as in the preparation of "garancine" from madder, showed that these preparations dyed exceedingly well when 1 per cent. of chalk was added to the dye-bath. It was found, for instance, that 7·5 grams of a sample of washed morinda root (equivalent to 10 grams of the unwashed root) had a dyeing power equal to 15 grams madder root of good quality.

The reds and pinks obtained on alumina mordant are yellower than the corresponding madder colours, the chocolate presents a similar difference in tone, and hence again appears fuller than a madder chocolate, whilst the lilac is distinctly redder. Oil-prepared calico mordanted as for turkey-red gives a very bright orange-red or scarlet similar in shade to that given by flavopurpurin, and fast to clearing with soap and stannous chloride. Chromium mordant on similarly prepared calico gives a full rich chocolate, and iron mordant yields colours varying from dull purple to black, according to the intensity of the mordant. On wool and silk, mordanted according to the usual methods, good chocolate-browns are obtained with chromium, orange-reds with alumina, bright orange with tin, and dark purple and black with iron mordant. All the colours referred to are as fast to soap as the corresponding madder colours. With respect to wool and silk in the unmordanted condition, these fibres may be readily dyed both with the washed and unwashed root, more or less rich orange or yellow colours, the brightness of which is enhanced by the addition of a little acetic acid to the dye-bath. These colours, however, which appear to originate from the glucoside morindin itself, are of a sensitive character towards alkalis and of little value.

MORINDA UMBELLATA OR MANG-KOUDU.

The dyeing material, variously named oungkoudou, jong-koutong, etc., is the root-bark of *Morinda umbellata* (Linn.) and is met with

in Eastern commerce in the form of small, reddish-brown, irregular rolls of bark, much wrinkled in appearance. Its cost is or was about 6d. per lb. In Java it is largely used for producing the fast reds in the native calico prints, well known under the name of "batticks".

Although the shrub from which the root-bark is obtained is met with in Ceylon and the hilly regions of Eastern, Southern, and South-Western India, as well as in the Malay Peninsula and Java, the material does not appear to be considered as of any special importance by the Hindoo dyers, unless, indeed, as is very probable, they use the root as a whole under the general designation "ál root," of which it must simply be regarded as a variety.

The following are a few of its Indian vernacular names: Ál (Bomb); núna (Tamil); múlúghúdú (Telugu); mang-kudu (Malay).

The older literature connected with mang-koudu is extremely limited, brief reference to its dyeing properties only being found in the following publications: "Philosophy of Permanent Colours" (1813), Bancroft; "Bulletin de la Société Industrielle de Mulhouse" (1832), E. Schwartz and D. Koechlin; "L'Art de la Teinture des Laines" (1849), Gonfreville; "Monograph on the Dyestuffs and Tanning Matters of India," etc. (1878), T. Wardle; Watt's "Dictionary of the Economic Products of India" (1891), J. Murray.

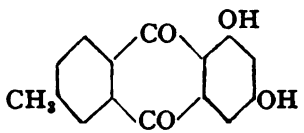
The examination of this dyestuff by Perkin and Hummel (Chem. Soc. Trans., 65, 851) has indicated its close chemical resemblance to the *Morinda citrifolia*. It contains a glucoside of the nature of morindin, which yields by hydrolysis morindon, but which, according to Perkin (Chem. Soc. Proc., 1908, 24, 149), is best represented by the formula $C_{26}H_{28}O_{14}$, and is identical with that suggested by Thorpe and Greenall (Chem. Soc. Trans., 1887, 51, 52) for the morindin derived from the *Morinda citrifolia*. The *acetyl* derivative $C_{26}H_{20}O_{14}(C_2H_3O)_8$ is very sparingly soluble in alcohol, and melts at 246—248°, and the sugar produced from the glucoside yields an osazone melting at 202—203°, which is not readily dissolved by alcohol.

This root-bark contains a considerable quantity of chlorogenin (cf. Madder), together with a small amount of non-tinctorial yellow derivatives of anthraquinone. A quantitative examination of the extract from 200 grams of the material with sulphurous acid (cf. Madder) gave 9·47 grams of green precipitate, which yielded:—

Crude chlororubin .	8·075 grams	= 4·03 per cent.
Pure morindon .	1·187 „	= 0·59 „ „
Yellow substances .	0·208 „	= 0·104 „ „

These yellow substances proved to consist of a mixture of at least six distinct compounds. The main constituent isolated in yellow needles, melting at 171—173°, possessed the formula $C_{16}H_{12}O_5$, and had properties in harmony with those required by a monomethyl ether of a trihydroxymethylanthraquinone. The diacetyl derivative $C_{16}H_{10}O_5(C_2H_3O)_2$ melts at 148°.

A second compound, $C_{15}H_{10}O_4$, crystallised in yellow needles, melting at 269°, and was found to consist of the *methylpurpuroxanthin* prepared synthetically (Marchlewski, Chem. Soc. Trans., 1893, 63, 1142) by the condensation of metadihydroxybenzoic acid with para-methylbenzoic acid—



The remaining yellow substances, (*a*) $C_{16}H_{12}O_6$, orange-red needles, melting-point 258°, (*b*) $C_{16}H_{10}O_5$, lemon-yellow needles, melting-point 198—199°, (*c*) $C_{16}H_{10}O_5$, needles, melting-point 208°, were isolated in such small amount that a determination of their constitution could not be attempted.

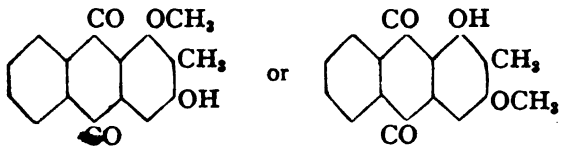
Dyeing Properties.—This dyestuff is largely employed by the Javanese for producing the fast reds in their celebrated "baticks". The colours it yields are practically identical with those given by morinda root, but much fuller, a fact not to be wondered at, for it is well known that in ordinary morinda root the colouring principle is situated chiefly in the root bark. In its ordinary condition mang-kudu is not useful in dyeing, but as in the case of ál root, a preliminary washing or steeping in water suffices to remove the deleterious acid principles present, and thus to transform it into a valuable red dyestuff.

MORINDA LONGIFLORA.

Morinda longiflora, known as "Ojuologbo" (woody vine) (Jour. Soc. of Arts, 1905, 53, 1069), is a native of West Africa, and considered to be one of the most valuable medicinal plants of that region. It is fully described in the "Flora of Tropical Africa" (1877, 111, 192), where it is stated to be known under the native name of "Mibogga".

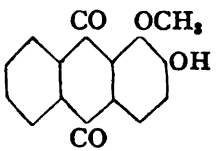
According to Barrowcliff and Tutin (Chem. Soc. Trans., 1907, 91, 1909) the root of the *Morinda longiflora* (G. Don) contains an *hydroxymethoxymethylanthraquinone* and an *alizarin-monomethyl*

ether, although morindin, the common constituent of the roots of the *Morinda citrifolia*, *Morinda tinctoria* and *Morinda umbellata*, is absent. The hydroxymethoxymethylanthraquinone, $C_{16}H_{12}O_4$, yellow needles, melts at 290°, and the acetyl derivative at 173°. Heated with 70 per cent. sulphuric acid it gives the 1 : 3-dihydroxy-2-methylanthraquinone of Schunck and Marchlewski (Chem. Soc. Trans., 1894, 65, 182). Accordingly it possesses one of the following formulæ—



Hydriodic acid converts it into dihydroxymethylanthranol, $C_{15}H_{12}O_3$ (melting-point 235°), and by methylation 1 : 3-dimethoxy-2-methyl anthraquinone (melting-point 181°) is produced.

The monomethyl ether of alizarin



is identical with the compound isolated by Perkin and Hummel (Chem. Soc. Trans., 1893, 63, 1174) from chay root, *Oldenlandia umbellata* (Linn.).

The leaves of the *Morinda longiflora* also contain the above-mentioned hydroxymethoxymethylanthraquinone, and in addition a crystalline alcohol *morindanol*, $C_{28}H_{62}O_4$, which melts at 278° and has $[a]_D$ + 65·9°. With sodium methoxide and methyl iodide it yields methyl morindanol, $C_{28}H_{61}O_3 . OCH_3$ (melting-point 116°).

"Ojuologbo" does not appear to contain an alkaloid, and extracts of the leaves and root were not found to possess any pronounced physiological action (B. and T.).

Rhubarb.

Probably no natural product has been so frequently examined as rhubarb root (*Rheum officinale*), but only those communications which appear to be of sufficient importance will be dealt with here. Geiger (Annalen, 1823, 8, 47; 1824, 9, 91) isolated from the root a substance, "rhabarberin," which he termed its most important constituent, in the form of small wart-like crystals, and this was later shown

by Schlossberger and Döpping (*ibid.*, 1844, 50, 214) to be identical with the chrysophanic acid described by Rochleder and Heldt (Ann. Chem. Pharm., 1843, 48, 12) as present in the wall lichen (*Parmelia parietina*). W. de la Rue and Müller by extracting the root (Chem. Soc. Trans., 1857, 10, 298) with benzene and treating the residue with sodium carbonate solution, separated it into two portions, namely, *chrysophanic acid*, which remains undissolved, and *emodin*, which passes into solution. Liebermann and Seidler (Annalen, 212, 36) by distilling chrysophanic acid with zinc-dust obtained methylanthracene, and gave it the constitution of a dihydroxymethylanthraquinone, and whereas emodin consisted of a trihydroxymethylanthraquinone (Liebermann, Annalen, 183, 176), it appeared that these compounds were related in the same way as purpurin and alizarin. Much more recently Hesse (Annalen, 1899, 309, 32) found that rhubarb contains *rhein*, and in addition to this isolated *rhabarberon*, isomeric with emodin, and a third compound containing a methoxy group presumably chrysophanic acid methyl ether. Eyken (Pharm. Weekblad, 1904, 41, 177), again, besides chrysophanic acid, emodin, and rhein, obtained *iso*-emodin, evidently identical with Hesse's rhabarberon, whereas Oesterle and Johann (Arch. Pharm., 1910, 248, 476) indicated that Hesse's third compound, containing a methoxy group, was the *emodin methyl ether* previously isolated by Tutin and Clewer from the *Rumex ecklonianus* (Meissner). This in reality was first described by Perkin and Hummel as present in the root-bark of the *Ventilago madraspatana* (Chem. Soc. Trans., 1894, 65, 940), and that of the *Polygonum cuspidatum* (*ibid.*, 67, 1084). That rhubarb contains glucosides was shown by Tschirch and Heuberger (Arch. Pharm., 1902, 204, 596), and one of these compounds, *chrysophanein*, a glucoside of chrysophanic acid, has been described by Gilson (Arch. Internat. de Pharmakadynamie et de Therapie, 1905, 487). The latest and most systematic examination of rhubarb root was carried out by Tutin and Clewer (Chem. Soc. Trans., 1911, 99, 946), who have shown that the *iso*-emodin of Tschirch and Eyken and the rhabarberon of Hesse consist of *aloe-emodin*, and moreover, in addition to these a fifth anthraquinone derivative, *rheinolic acid*, is also present. Rhein, emodin, aloe-emodin, emodin monomethyl ether, and chrysophanic acid exist in the root partly in the form of glucoside, though it was not found possible by these authors to separate the individual constituents of this glucoside mixture. More recently the interesting discovery has been made by Müller (Trans. Chem. Soc., 1911, 96, 967) that *alizarin* is present in this drug. Rhubarb root contains also gallic acid, cinnamic acid, and a non-glucosidic resin,

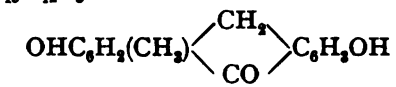
to which latter the purgative actions of this drug are mainly due. On the other hand, emodin and chrysophanic acid possess this property in a mild degree.

CHRYSOPHANIC ACID.—Chrysophanic acid, $C_{15}H_{10}O_4$, as obtained from rhubarb is contaminated with emodin methyl ether which is difficult to remove by fractional crystallisation, and on this account a considerable variation in its melting-point is to be observed in the earlier literature. The difficulty in removing the emodin methyl ether can be overcome according to Oesterle (Arch. Pharm., 1905, 243, 434) by heating the crude substance in benzene solution with aluminium chloride. This demethylates the emodin which can then readily be eliminated by crystallisation and the pure chrysophanic acid isolated in brownish-yellow leaflets, melting-point 196° (Tutin and Clewer, *loc. cit.*). Chrysophanic acid is insoluble in cold solutions of the alkali carbonates, but dissolves in dilute caustic alkalis with a cherry-red colour, and from this solution the calcium salt is deposited by addition of lime water. Distilled, as already indicated, with zinc-dust it yields, according to Liebermann and Seidler, β-methylanthracene, but according to Jowett and Potter (Chem. Soc. Trans., 1903, 83, 1327), owing to the great similarity which exists between the isomeric methylanthracenes, this cannot be regarded as proven.

Acetylation gives first *monoacetylchrysophanic acid*, $C_{15}H_9O_4$, (C_2H_3O), yellow needles, melting-point 152° (Hesse, *loc. cit.*), and subsequently *diacetyl chrysophanic acid* leaflets, first obtained by Liebermann, and which, according to Oesterle, melts at 208°. *Dibenzoylchrysophanic acid* is described by Warren de la Rue and Müller (Jahres., 1862, 323) as prisms, melting-point 200°, and by Tutin and Clewer as pale yellow needles, melting-point 204°. Chrysophanic acid is not methylated by means of sodium and methylic iodide at 100° (Jowett and Potter), but with methyl sulphate it gives first *chrysophanic acid monomethyl ether*, $C_{15}H_9O_3(OCH_3)$, orange-coloured needles, melting-point 204°, which forms the acetyl derivative, melting-point 204—205°, and subsequently *chrysophanic acid dimethyl ether*, $C_{14}H_5O_2CH_3(OCH_3)_2$, needles, melting-point 195°. According, however, to Tutin and Clewer (Chem. Soc. Trans., 1910, 97, 6) with methyl iodide and sodium methylate in presence of alcohol, at 100° the dimethyl ether can be obtained.

By heating with fuming nitric acid, chrysophanic acid gives the *tetra-nitro compound*, $C_{15}H_6O_4(NO_2)_4$ (Liebermann and Giesel, Annalen, 183, 175), yellow leaflets or needles which yield crystalline salts of the type $C_{15}H_4N_4O_{12}K_2$. Strong ammonia at 200° gives *amino-chryso-*

phanic acid, $CH_3C_{14}H_5OH(NH_2)O_2$, small brown leaflets (Liebermann and Giesel); Hesse obtained the same compound by the action of strong ammonia in the cold (Annalen, 1899, 309, 32). By adding tin to a boiling solution of chrysophanic acid in acetic acid and subsequently fuming hydrochloric acid, or by boiling chrysophanic acid with zinc-dust, Liebermann (Ber., 21, 436) obtained *chrysophanhydranthrone*, $C_{15}H_{12}O_3$—

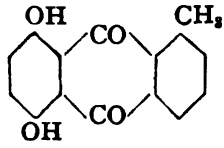


yellow leaflets, melting-point 196°, which gave an acetyl compound, melting-point 230—231°. By the action of hydriodic acid Hesse obtained the same substance (Annalen, 284, 194), and this product, no doubt *methyl-dihydroxy-anthranol*, was considered by Jowett and Potter (Chem. Soc. Trans., 1902, 1528) to be identical with the chrysarobin of Goa powder. By oxidation it is reconverted into chrysophanic acid. Gilson isolated from Chinese rhubarb (Arch. Internat. de Pharmakadynamie et de Therapie, 1905, xiv., 487) a glucoside of chrysophanic acid which he termed *chrysophanein*.

This crystallises in yellow needles, melting-point 242—249°, insoluble in dilute ammonia, but soluble in sodium hydrate solution with a reddish-brown coloration. By hydrolysis with acids it is converted into chrysophanic acid and glucose—

$$C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_4 + C_6H_{12}O_6$$

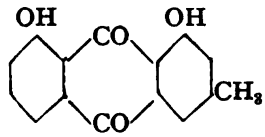
Though chrysophanic acid is evidently a dihydroxymethyl-anthraquinone its exact constitution has long been uncertain as attempts to synthesise it have at present failed. By fusion with alkali or oxidation with permanganate, benzoic acid is not produced, and consequently the methyl and the two hydroxyl groups are not all present in the same benzene nucleus (Jowett and Potter). These authors and Hesse (Annalen, 1899, 309, 32) assign to chrysophanic acid the constitution of a methyl quinizarine—



Against this, which would, however, explain Jowett and Potter's statement as to its non-methylation by means of methylic iodide, is the fact that in its colour reactions chrysophanic acid does not resemble quinizarine itself. Oesterle (Chemie der natürlichen Farbstoffe, Rüpe,

2, 117) favours the view of Liebermann that this compound is a β-methylanthraquinone derivative and represents it as a β-methyl 1·8 or 1·6 dihydroxy anthraquinone of which he indicates five distinct possibilities.

More recently, however, Leger (J. Pharm. Chim., 1912, 5, 281) has assigned to chrysophanic acid the constitution of a 1·8 dihydroxy-methylanthraquinone, and this is doubtless correct—



Interesting is the fact described by Oesterle (Arch. Pharm., 1908, 249, 455) that chrysophanic acid can be oxidised to rhein, and that when aloe-emodin is reduced chrysophanic acid is obtained.

Though chrysophanic acid has long been considered as devoid of tinctorial property, according to Rüpe (*loc. cit.*) this is incorrect.

By employing mordanted and unmordanted wool the following shades may be obtained :—

Aluminium.	*Chromium.*	*Without Mordant.*
Red-yellow.	Dull yellow.	Citron-yellow.

As already indicated, chrysophanic acid is present in the lichen *Parmelia parietina*, and among other sources are the *Squamaria elegans* (Thomson, Annalen, 53, 260), the root of the *Rumex obtusifolius* (Thann, Annalen, 1858, 107, 324), *Rumex ecklonianus* (Tutin and Clewer, Chem. Soc. Trans., 1910, 97, 1), *Rumex nepalensis* (Hesse, Annalen d. Chemie u. Pharmacie, 1896, 291, 306), *Cascara sagrada* (Leprince, Comptes rend., 1899, 129, 60), and in the bark of the *Rhamnus frangula* (Limousin, J. Pharm. Chim., 1885, 80).

EMODIN, $C_{15}H_{10}O_5$.—Emodin, the second important constituent of rhubarb root, is now known as *frangula-emodin* not only on account of its existence (in the form of glucoside) in the bark of the *Rhamnus frangula*, but to distinguish it from the isomeric *aloe-emodin* which can be obtained from rhubarb and other sources.

It was first isolated from rhubarb root by Warren de la Rue and Müller (Trans. Chem. Soc., 1857, 10, 300), who extracted the washed root with benzene, and treated the crude mixture of emodin and chrysophanic acid thus isolated with sodium carbonate solution, in which, in the cold, emodin only is soluble.

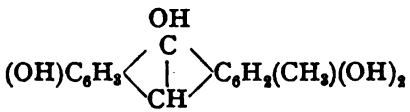
Emodin crystallises in orange-red needles sparingly soluble in benzene, more readily soluble in alcohol, it melts at 254—255°

(Perkin, Chem. Soc. Trans., 67, 1086), 252° (Tutin and Clewer), 250° (Oesterle, *loc. cit.*). Solutions of the alkaline hydrates and ammonia dissolve it with a violet-red colour and sulphuric acid with a deep red tint. Distilled with zinc-dust it yields methyl anthracene which according to Oesterle and Tisza (Arch. Pharm., 1908, 246, 432) is the *β* variety.

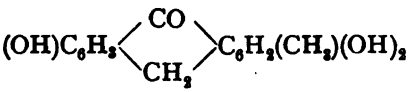
Triacetyl-emodin, $C_{15}H_7O_5(C_2H_3O)_3$, long yellow needles, melts at 196—197°; *Tripropionyl-emodin*, needles, at 121—123°, and *Dibenzoyl-emodin*, needles, at 223—224° (Oesterle and Tisza). *Emodin tridiphenyl urethrane* (Tutin and Clewer, Chem. Soc. Trans., 1912, 101, 290), $CH_3 . C_{14}H_4O_5(CO . NPh_2)_3$, crystallises in pale yellow prisms, melting-point 193°.

Methylation by means of methyl sulphate gives *Emodin trimethyl ether* needles, melting-point 225° (Oesterle and Tisza).

When reduced in boiling acetic acid solution with tin in a finely divided condition emodin yields *Emodin anthranol*—



which may also be represented as



It forms colourless crystals, soluble in ammonia and barium hydrate solutions with a yellowish-brown colour.

Emodin is thus a *trihydroxymethylanthraquinone* and may consist, as Liebermann suggests, of an hydroxychrysophanic acid. If this is admitted, there can be little doubt that the third hydroxyl is in the meta position to one of the others present in chrysophanic acid, and it will consequently consist of an *hydroxymethylpurpuroxanthin.*

Emodin is contained as the glucoside *frangulin* in the bark of the *Rhamnus frangula*, the glucoside *polygonin* in the root of the *Polygonum cuspidatum*, and it has also been isolated from the *R. purshianos* and *R. cuilludica* (Tschirch and Pool, Arch. Pharm., 1908, 246, 315) and *R. cathartica* (Tschirch and Polacco, Arch. Pharm., 1900, 238, 459).

FRANGULA-EMODIN METHYL ETHER.—This compound, as already stated, is found associated with crude chrysophanic acid, and to its contamination with this impurity is to be ascribed the lower melting-

point at first assigned to this latter substance. Originally isolated by Perkin and Hummel (Trans. Chem. Soc., 1894, 65, 632) from the root-bark of the *Ventilago madraspatana* and by Perkin from the root of the *Polygonum cuspidatum* (*ibid.*, 67, 1084), it was identified by Tutin and Clewer (*ibid.*, 1910, 97, 1) as one of the constituents of the *Rumex ecklonianus*. Jowett and Potter (*ibid.*, 1903, 77, 1330) who prepared this compound by the methylation of emodin doubted at first the identity of their product with the natural compound, but somewhat later Tutin and Clewer (*loc. cit.*) proved this to be the case.

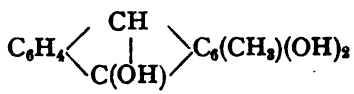
It can be isolated (Oesterle and Johann, Arch. Pharm., 1910, 248, 476) by extracting the acetylated crude chrysophanic acid with alcohol at 50—55°, and hydrolysing the acetylemodin methyl ether thus produced, and has also been obtained (Tutin and Clewer) by a fractional extraction of the constituents of rhubarb root. The properties of this compound, which crystallises in orange-red needles, are described later in connection with the root-bark of the *Ventilago madraspatana*.

According to Oesterle and Johann this emodin methyl ether is identical with Gilson's rheo-chrysidin (Arch. internat. Pharm. Ther., 1905, 14, 492), with Hesse's physcion (lichen-chrysophanic acid) (Abst., 1906, 1, 280), and with the methyl-chrysophanic acid of this latter author (Abst., 1900, 1, 41).

ALOE-EMODIN.—Aloe-emodin appears to have been first isolated from rhubarb by Hesse (Pharm. J., 1895, iv., 1, 352, and Annalen, 1899, 309, 32), who described it as *rhabarberon* isomeric with emodin, $C_{15}H_{10}O_5$, and subsequently by Eyken who, though considering it as probably identical with Hesse's rhabarberon, termed it *iso*-emodin. More recent work by Oesterle has shown (Arch. Pharm., 1899, 88) that historically the first preparation of this compound, though in an impure condition, is due to Tilden (Chem. Soc. Trans., 1877, 267), who under the name of aloe-chrysin obtained it by the oxidation of aloin (see later). Tutin and Clewer (*ibid.*, 1911, 948), on the other hand, first recorded aloe-emodin as a constituent of rhubarb root, and at the same time confirmed the identity of rhabarberon, iso-emodin, and aloe-emodin. According to Oesterle (*loc. cit.*) the emodin existing in senna is also aloe-emodin. Aloe-emodin crystallises in pale brown orange needles melting at 223—224°, soluble in dilute ammonia to form a red-coloured liquid and in sulphuric acid with the same tint. These properties are identical with those of frangula-emodin, but on heating their solutions in sulphuric acid the product thus given by aloe-emodin dissolves in ammonia with a violet, whereas that from frangula-emodin gives a red coloration.

Acetylaloe-emodin, $C_{15}H_8O_5(C_2H_3O)_2$, yellow needles, melts at 177—178° (Oesterle, Arch. Pharm., 1899, 237, (2), 81, 699), *tripropionyl aloe-emodin*, needles, at 152—153° (Oesterle), and *tribenzoyl aloe-emodin*, greenish-yellow needles, at 234° (Robinson and Simonsen, Chem. Soc. Trans., 1909, 95, 1091). According to Leger (Comptes rend., 1910, 151, 128) *tetranitroaloe-emodin*, $C_{15}H_6O_5(NO_2)_4$, forms golden needles, melting-point 285°.

By the reduction of aloe-emodin with tin and hydrochloric acid in the presence of acetic acid, Oesterle (Schweiz. Wochenschr. f. Chem. u. Pharm., 1900, 21) obtained a compound crystallising in yellowish-green leaflets, melting-point 181—187°, which possessed the formula $C_{15}H_{12}O_3$ and was regarded as a dihydroxymethylanthranol—



By oxidation with chromic acid aloe-emodin is converted into rhein (Oesterle, Arch. Pharm., 1903, 241, 604), and when reduced chrysophanic acid is obtained (Oesterle, Arch. Pharm., 1911, 249, 455). The constitution of aloe-emodin is given on page 59.

Rhein.

Rhein was isolated from rhubarb by Hesse (Annalen, 1899, 309, 43), whereas Oesterle and Babel (Schweiz. Woch. Chem. Pharm., 1904, 42, 329) showed that Tilden's aloe-xanthin prepared by the oxidation of barbaloin, and to which he had assigned the formula $C_{15}H_{10}O_6$, was a mixture of aloe-emodin and rhein. More recently its presence in rhubarb root has been confirmed by Tutin and Clewer (*loc. cit.*). It crystallises from pyridine in glistening orange-yellow needles melting at 318° (Tutin and Clewer), 314° (Oesterle), and is soluble in dilute alkaline solutions with a red colour. According to Oesterle it possesses well-defined tinctorial property and gives on fabrics mordanted with aluminium and chromium yellow shades.

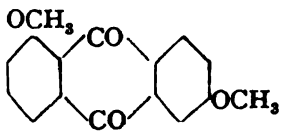
The relationship between aloe-emodin and rhein and the constitution of these compounds has been elucidated by Robinson and Simonsen (Chem. Soc. Trans., 1909, 95, 1085). Whereas rhein yields only a diacetyl compound, and this is soluble in sodium acetate solution, further proof of the presence of a carboxyl group is afforded by the fact that this substance on hydrolysis and esterification readily yields an ester, which by saponification is again converted into rhein. As aloe-emodin $C_{15}H_{10}O_5$ containing three hydroxyl groups is converted by oxidation with chromic acid into rhein $C_{15}H_6O_4(OH)_2$ in which but two are present, it is clear that one of the hydroxyls of

aloe-emodin must be contained in a CH_2OH group and the oxidation process be represented as follows :—

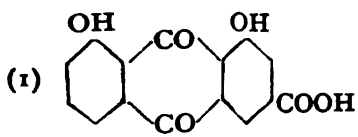
$$C_{14}H_5O_2(OH)_2CH_2OH + O_2 = C_{14}H_5O_2(OH)_2COOH + H_2O$$

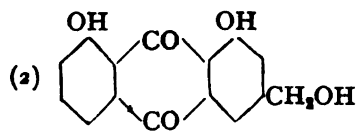
Aloe-emodin is thus the carbinol and rhein the corresponding carboxylic acid of a dihydroxy-anthraquinone.

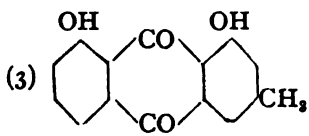
To obtain an insight into the nature of this latter, Robinson and Simonsen prepared its dimethoxy derivative by converting *dimethyl rhein amide*, $C_{14}H_5O_2(OMe)_2CONH_2$, into *amino-dimethoxy-anthraquinone*, $C_{14}H_5O_2(OMe)_2NH_2$, and then eliminating the amino group in the usual way. The properties of this dimethoxy compound, according to these authors, indicate it to consist of iso-chrysazin dimethyl ether—



The constitutions of rhein (1), aloe-emodin (2), and chrysophanic acid (3) may therefore be expressed thus :—







The following derivatives of rhein have been obtained :—

Diacetyl-rhein, $C_{15}H_6(C_2H_3O)_2O_6$, needles, melting-point 247—248° (Oesterle), 258° (Tutin and Clewer), *Tetranitro-rhein* (Leger), $C_{15}H_4O_6(NO_2)_4$, short efflorescent prisms, *Rhein ethyl ester*, $C_{14}H_5O_2(OH)_2COOEt$, needles, melting-point 159°, *Diacetyl-rhein ethyl ester*, plates, melting-point 170°, *Rhein dimethyl ether*, $C_{14}H_5O_2(OMe)_2COOH$, light-brown needles, melting-point 283—284°, *Dimethyl rhein ethyl ester*, $C_{14}H_5O_2(OMe)_2COOEt$, sulphur-yellow needles, melting-point 185—187°, *Dimethyl rhein chloride*, $C_{14}H_5O_2(OMe)_2COCl$, yellow prisms, melting-point 190°, *Dimethyl rhein amide*, $C_{14}H_5O_2(OMe)_2CONH_2$,

plates, melting-point 287° (Robinson and Simonsen). The amino-dimethoxy-anthraquinone and dimethoxy-anthraquinone alluded to above melt respectively at 243° and 204—205°.

RHEINOLIC ACID.—This compound, which is present in rhubarb root only in very small amount, was discovered by Tutin and Clewer (*loc. cit.*) in the mother liquor obtained during the purification of their emodin. Crystallised from pyridine it forms dark-red lustrous needles, which after drying at 130° melted between 295—297°.

Rheinolic acid, $C_{17}H_{10}O_6$, is a carboxylic acid containing at least one hydroxyl group, and when acetylated yields *acetylrheinolic acid*, small orange-coloured needles, melting at 236°, which readily dissolve in cold aqueous sodium carbonate. It is evidently an anthraquinone derivative, probably structurally related to rhein, and according to the above authors may contain a bridged ring. Alkaline solutions and concentrated sulphuric acid dissolve it with an intense red colour, and it is distinguished from rhein by the fact that addition of water does not precipitate it from its solution in the latter solvent.

ALIZARIN.—The presence of this substance in rhubarb root has been demonstrated by Hugo Müller (Chem. Soc. Trans., 1911, 96, 967) who isolated it from the residue which accumulates during the preparation of the officinal aqueous extract of rhubarb. This was extracted with benzene, and the product thus obtained fractionally crystallised from the same solvent. The alizarin in these circumstances is much less soluble than the emodin and chrysophanic acid which accompany it. The quantity present in the root is apparently minute.

RUMEX ECKLONIANUS.

Rumex ecklonianus (Meisner) is a herb indigenous to South Africa which possesses medicinal properties of a mild purgative nature. Tutin and Clewer (Chem. Soc. Trans., 1910, 97, 6) examined the over-ground portion of the plant, and found it to contain *chrysophanic acid*, *emodin*, *emodin mono-methyl ether* and *kaempferol*.

RUMEX NEPALENSIS.

According to Hesse, the root of *Rumex nepalensis* (Wall), does not contain chrysophanic acid, but there is present in addition to two other substances, one he termed rumicin, which is isomeric with it.

Rumicin, $C_{15}H_{10}O_4$, golden-yellow leaflets, melts at 186—188°, and is soluble in caustic potash solution with a purple-red coloration. With hydriodic acid it yields chrysophanohydranthrone.

Nepalin, $C_{17}H_{14}O_4$, orange needles, melts at 136°, is insoluble in alkali carbonates, but dissolves in caustic potash, forming a purple

solution. *Diacetyl-nepalin*, $C_{17}H_{12}O_4(C_2H_3O)_2$, crystallises in brownish-red rhombohedra, melting-point 181°.

Nepodin, the main constituent of the root $C_{18}H_{16}O_4$, greenish-yellow prisms, melting-point 158°, is distinguished from the preceding compounds by its solubility in solutions of the alkali carbonates. The *diacetyl* compound forms pale yellow rhombohedra which darken at 180°, and melt with decomposition at 198°.

Senna Leaves.

Senna consists of the leaves of various species of *cassia* which are employed in medicine on account of their purgative properties. It has been the subject of numerous investigations and was long reputed to contain chrysophanic acid.

According to Tschirch and Hiepe (Arch. Pharm., 1900, 238, 427), these leaves contain *gluco-sennin*, a yellow crystalline substance, probably a glucoside of emodin, *senna-emodin*, $C_{15}H_{10}O_5$, melting-point 223—224°, *senna-iso-emodin*, $C_{15}H_{10}O_5$, and *senna-chrysophanic acid*, $C_{15}H_{10}O_4$, which melts at 223—224°. *Senna-rhamnetin*, yellow needles, which does not melt below 260°, and a substance $C_{14}H_{10}O_5$ are also present. Tutin (Chem. Soc. Trans., 1913, 103, 2006), who examined Tinnevelly, Lima and Peru senna leaves, *C. angustifolia* (Vahl), and the Alexandrian senna leaves, *C. acutifolia* (Delile), could not confirm the statements of Tschirch and Hiepe as to the presence of senna-iso-emodin or senna-chrysophanic acid.

The anthraquinone derivatives isolated consisted solely of *aloe-emodin*, $C_{15}H_{10}O_5$, and *rhein*, $C_{15}H_8O_6$, and these were present partly in the free condition and partly as glucosides. Senna leaves also contain *kaempferol*, $C_{15}H_{10}O_6$ (see *Delphinium consolida*), and a new glucoside of this substance, *kaempferin*, $C_{27}H_{30}O_{16}6H_2O$, melting-point 185—195°. In addition to the above-mentioned compounds, the senna leaves from Lima and Peru contained *isorhamnetin*, $C_{16}H_{12}O_7$, identical with that first isolated by Perkin from the yellow wallflower (Chem. Soc. Trans., 1896, 69, 1658), and this is probably the so-called senna-rhamnetin of Tschirch and Hiepe.

Rhamnus frangula.

The bark of the alder buckthorn, *R. frangula* (Linn.), a shrub widely distributed throughout Europe, is employed in medicine chiefly in the form of a fluid extract as a mild purgative. Since the beginning of the last century the bark of this plant has been submitted to repeated examination, but an account of the earliest re-

searches need not be recorded here. Casselmann (Annalen, 1857, 104, 77) was the first to analyse its main crystalline constituent which he termed *frangulin*, and this he extracted from the bark by means of ammonia. Faust (Annalen, 1872, 165, 229) by the hydrolysis of frangulin with hydrochloric acid obtained, in addition to a sugar, a substance he termed *frangulic acid*, and as by the distillation of this compound with zinc-dust anthracene was produced he concluded it to be a dihydroxy-anthraquinone isomeric with alizarin.

Liebermann and Waldstein did not prepare frangulin (Ber., 1876, 1775) but studied the colouring matter obtained from the bark by means of caustic soda solution, evidently the same substance as Faust's frangulic acid. This they isolated by sublimation and found to consist of emodin, and suggested that the hydrolysis of frangulin with acids might probably be represented by the following equation :—

$$C_{21}H_{20}O_{10} + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_6$$

Faust (Pharm. Zeitschrift für Russland, 17, 257), on the other hand, considered that Liebermann and Waldstein's compound was not in reality emodin but rather a trihydroxydimethyl or a trihydroxyethyl-anthraquinone.

The subject was next studied by Schwabe (Arch. Pharm., 1888, 26, 259), who devoted special attention to frangulin. To this he assigned the formula $C_{21}H_{20}O_9$, and obtained from it by hydrolysis emodin and a sugar. This latter, which he did not isolate in a pure condition, he regarded as the rhamnodulcite of Liebermann. Finally Thorpe and Robinson (Chem. Soc. Trans., 1890, 57, 38) and Thorpe and Miller (*ibid.*, 1892, 61, 1) submitted frangulin to detailed examination, and showed that, as Schwabe had stated, its correct formula is $C_{21}H_{20}O_9$. When hydrolysed it yields emodin, and rhamnose, which was isolated in a crystalline condition, and as a result the reaction may be thus expressed :—

$$C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_5$$

For the preparation of frangulin the crushed bark is first treated with ligroin to remove wax and chlorophyll and subsequently extracted with alcohol. The extract is evaporated to dryness with sand, the powdered product extracted with ether, and after distilling off the ether the residue is treated with a little alcohol. On standing the solution deposits a mixture of emodin and frangulin together with a small quantity of a more sparingly soluble substance, and these can be separated by fractional crystallisation from alcohol.

Frangulin is an orange-yellow crystalline powder sparingly soluble in alcohol and melts at about 225°. It is readily susceptible to hydrolysis, and this indeed occurs to a slight extent by mere boiling with alcohol.

The sparingly soluble substance which contaminates the crude frangulin, the presence of which was also observed by Schwabe, crystallises from alcohol in golden-yellow needles, melting at 202—203°. It dissolves in sulphuric acid with a red coloration, in dilute alkalis with the same tint, and is almost insoluble in ammonia. It appears to possess the formula $C_{15}H_{10}O_5$, being thus isomeric with emodin, though Perkin (Chem. Soc. Trans., 1895, 67, 1084) has suggested its possible identity with the emodin methyl ether $C_{16}H_{12}O_5$ of the *Ventilago madraspatana* and *Polygonum cuspidatum*, with which in melting-point and property it closely agrees.

POLYGONUM CUSPIDATUM.

P. cuspidatum (Sieb. et Zucc.) is common in India, China, and Japan, and is referred to by A. Henry in a paper entitled "Chinese Names of Plants" (Journal Royal China Branch of Royal Asiatic Society, 22, New Series, No. 5, 1887) as "Kan-yen, wu-tzu," the name employed at Patung for its root, which is said to be used for dyeing yellow.

According to Perkin (Chem. Soc. Trans., 1895, 67, 1084) the main constituent of this root is a glucoside, *polygonin*, $C_{21}H_{20}O_{10}$, forming orange-yellow needles, melting-point 202—203°, which, when hydrolysed by acids, gives emodin and a sugar :—

$$C_{21}H_{20}O_{10} + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_6$$

A trace of a second glucoside is also present, from which the emodin monomethylether, melting-point 200°, previously found to exist in the root-bark of the *Ventilago madraspatana* (Gaertn.) (Chem. Soc. Trans., 1894, 65, 932), was obtained.

ALOES.

Aloes consist of an exudation from the leaves of various species of aloe, which has been evaporated to dryness. The leaves of the aloe plants are fleshy and contain a bitter resinous juice, which exudes when they are cut transversely. This is collected and is allowed to dry gradually at the ordinary temperature, or more frequently is boiled until a sample on cooling sets to a solid mass. In the former case the product is opaque owing to the presence of crystals of aloin, whereas in the latter, these being absent, it is vitreous and transparent. Aloes are employed medicinally as a

purgative and form one of the commonest constituents of pills and aperients generally. The chief varieties of aloes are Barbadoes aloes, *A. arborescens*, Socrotine aloes, *A. socrotina*, and Cape aloes, *A. ferox*, *A. arborescens*, *A. perryi* (Baker). Uganda aloes are a variety of Cape aloes. Natal aloes are not now found in commerce. Finally, Curaçoa aloes are prepared from the *A. vulgaris*, *A. socrotina*, and *A. arborescens*, Jafferabad aloes from *A. abyssinica*.

Though aloes do not appear to have been employed to any extent for dyeing purposes, they give on fabrics mordanted with aluminium and iron a nut-brown coloured shade. More useful for this purpose in the past were the products of their decomposition with nitric acid known as *aloetic* and *chrysaminic acids*, substances studied by Schunck as far back as 1841 (Annalen, 39, 5). The first attempts to apply them to fabrics were made by Boutin in 1840. Aloetic acid dyes unmordanted wool a deep brown colour, and this is brightened by a subsequent treatment of the material in a bath of stannous chloride, whereas a moss-green shade is said to be obtainable by the use of ammonium aloetate. Chrysaminic acid also dyes wool brown, and the colour is rendered more permanent by the employment of aluminium and tin mordants. The literature on aloes is exceedingly voluminous, and on this account some part of the earlier work on this subject has been omitted.

Barbaloin.

Barbaloin was apparently first isolated from Barbadoes aloes by Smith (Jahresbericht, 1850, 545), and later investigated by Groves (*ibid.*, 1856, 680) and by Stenhouse (Phil. Mag., 1850, [iii.], 37, 481), the last-named of whom assigned to it the formula $C_{17}H_{18}O_7$. Rochleder and Czumpelik (Jahresbericht, 1863, 598) studied the action of alcoholic hydrochloric acid on aloin, and obtained in this manner a yellow crystalline substance which they termed *aloetin*, and a sugar, results suggesting that aloin was a glucoside. Hlasiwetz (Annalen, 1865, 134, 287) by alkali fusion obtained orcin, *p*-oxybenzoic acid, and a substance he termed *aloretic acid*, and Graebe and Liebermann (Ber., 1868, 1, 105) studied the products of its distillation with zinc-dust. These they proved to consist of anthracene and methylanthracene, and came to the conclusion that not only was aloin derived from one of these hydrocarbons, but chrysaminic acid obtained from it by the action of nitric acid $C_{14}H_4(NO_2)_4(OH)_2O_2$ was in reality a tetranitrodihydroxyanthraquinone.

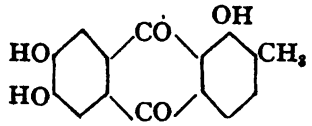
Tilden, who examined this subject in some detail (Chem. Soc.

Trans., 1872, 25, 204; 1875, 28, 1275; 1877, 32, 267), assigned to barbaloin the formula $C_{16}H_{18}O_7$, and prepared from it a crystalline trichloro derivative and an amorphous acetyl compound. The products of the action of nitric acid were oxalic, picric, aloetic, and chrysaminic acids, and again it was observed that aloetic acid by the further action of nitric acid gives chrysaminic acid. Tilden was the first to study the oxidation of aloin with chromic acid, and found that in this way *aloexanthin*, $C_{15}H_{10}O_6$, now known as rhein, is produced, this being probably a tetrahydroxymethyl-anthraquinone $C_{14}H_5Me(OH)_4O_2$. By the action of nitric acid on aloexanthin, chrysaminic acid was produced, and it appeared likely that Schunck's aloetic acid was trinitro-aloexanthin.

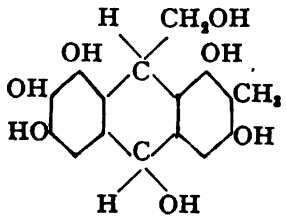
Though Schmidt (Ber., 1875, 8, 1275) adopted Tilden's formula $C_{16}H_{18}O_7$ for barbaloin, Groenewald (Arch. Pharm., 1890, 228, 115) and Leger (Comptes rend., 1897, 125, 185) proposed for it $C_{16}H_{16}O_7$. More recently, however, the latter author (*loc. cit.*) has considered the expression $C_{21}H_{20}O_9$ as more correct.

Tschirch and Pedersen (Arch. Pharm., 1898, 236, 200) by submitting barbaloin to aerial oxidation isolated aloe-emodin $C_{15}H_{10}O_5$, and proposed both for this (1) and for aloin (2) the following constitutions:—

(1)

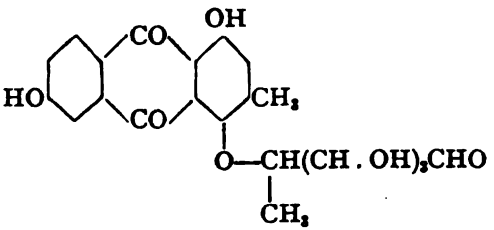


(2)



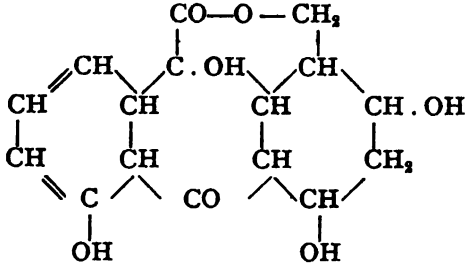
In these formulæ the positions of the hydroxyl groups were, however, uncertain. Oesterle (*ibid.*, 1899, 237, 81) somewhat later succeeded in preparing aloe-emodin from barbaloin by the prolonged action of alcoholic hydrogen chloride, and from this by oxidation with chromic acid Tilden's aloe-xanthin ("rhein") could be obtained.

Leger in 1902 (Comptes rend., 134, 1111, 1584) oxidised barbaloin with sodium peroxide, and in this way isolated aloe-emodin, formic acid, and an aldopentose. As, contrary to the statement of Rochleder and Czumpelik (*loc. cit.*), barbaloin is not hydrolysed with dilute acids or with alcoholic hydrochloric acid (Tschirch and Pedersen, *loc. cit.*), Leger regarded it in the light of these results as a new type of stable glucoside, and suggested for it the following constitution:—



This aldopentose he at first termed *Aloinose* (J. Pharm. Chim., 1904, vi., 20, 145), and stated that a crystalline osazone can be prepared from it.

Aschan (*ibid.*, 1903, 241, 341), on the other hand, determined the molecular weight of barbaloin by means of boiling acetone and obtained results in harmony with the older formula $C_{16}H_{18}O_7$ or $C_{16}H_{16}O_7$. Jowett and Potter, again (Chem. Soc. Trans., 1905, 87, 881), adopted the freezing-point method, and employing phenol as a solvent, both with barbaloin and tribrombarbaloin, came to the same conclusion. When acetylated tribrombarbaloin gave a tetra-acetyl derivative, indicating that barbaloin $C_{16}H_{18}O_7$ contains four hydroxyl groups. Robinson and Simonsen (*ibid.*, 1909, 95, 1085) studied the oxidation of acetylbarbaloin with chromic acid, and found that in this manner an excellent yield of diacetyl-rhein together with some acetyl-aloe-emodin can be obtained. Having ascertained the general constitution of both aloe-emodin and rhein (see Rhubarb), they came to the conclusion, in the light of Jowett and Potter's results, that the following formula could be tentatively assigned to barbaloin :—

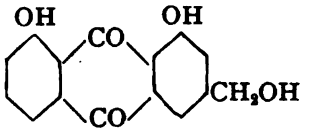


In 1910 Leger (Comptes rend., 150, 983, and *ibid.*, 1695, and J. Pharm. Chim., 1911, 4, 241) gave further details for the preparation of aloinose from barbaloin, and pointed out that this was identical with *d*-arabinose. In a later paper (*ibid.*, 151, 1128) it was shown also that the formation of chrysaminic and picric acids from aloin by means of nitric acid is preceded by that of tetra-nitro-aloe-

emodin, $C_{15}H_6O_5(NO_2)_4$, 2 : 4 : 6 trinitro 3 hydroxybenzoic acid being simultaneously produced. Tetra-nitro rhein,

$$C_{14}HO_2(NO_2)_4(OH)_2COOH,$$

again, is probably an intermediate product in the formation of chrysaminic acid from tetra-nitro-aloin, and these results are considered to harmonise with the glucosoidal nature of the aloins. Dextro-arabinose attached to the hydroxyl of aloe-emodin in position 1 constitutes barbaloin, whereas, when attached to the hydroxyl in position 8, the product is iso-barbaloin, aloe-emodin itself (see Rhubarb) being



By heating to 160—165° for three hours (Leger, Comptes rend., 1907, 145, 1179), barbaloin is partially converted into an amorphous optical isomeride *β-barbaloin*, which yields a chloro derivative $C_{21}H_{16}O_9Cl_4$, $5H_2O$, prismatic needles, and a bromo compound $C_{21}H_{16}O_9Br_4$.

By the action of acetic anhydride and sodium acetate at 100—110° for an hour, barbaloin gives *penta-acetyl-barbaloin* and *penta-acetyl β-barbaloin* (*ibid.*, 1914, 158, 1903). On saponification and crystallisation of the product from a mixture of chloroform and methyl alcohol, barbaloin is deposited first, whereas β-barbaloin, which can be obtained as an amorphous powder, remains in solution.

By directly chlorinating Cape or Uganda aloes (*ibid.*, 1908, 147, 806) a compound $C_{11}H_4O_3Cl_4$, melting-point 268—269°, crystallising in colourless needles, and which gives the *monoacetyl* derivative, melting-point 125°, is produced, which is the chloro derivative of a new phenol termed *aloesol*. By reduction with zinc and acetic acid, this is transformed into *tetra-hydro-dichlor-aloesol*, $C_{11}H_8O_3Cl_2$, melting-point 275°, the *acetyl* compound of which melts at 150—151°. By the action of nitric acid *tetrachloro-aloesol* gives oxalic acid and tetrachloro-quinone.

According to Tutin and Naunton (Pharm. J., 1914, (4), 37, 836), the statement of Tschirch and Pedersen (*loc. cit.*) that aloe-emodin is obtained by passing air through an alkaline solution of barbaloin is incorrect, and this observation would appear to be due to the contamination of their aloin with aloe-emodin itself, which indeed is frequently associated with it.

Seel and Kleber (Ber., 1916, 49, 364) determined the molecular weight of barbaloin by means of boiling acetone and boiling alcohol.

The results obtained were respectively 408 and 440, and appeared to confirm the belief of Leger that barbaloin has the formula $C_{21}H_{20}O_9$, rather than $C_{16}H_{18}O_7$, as suggested by Tilden.

Barbaloin can be readily prepared (Smith, *loc. cit.*) by extracting the aloes with two parts of water at 90—95°, and the crystals which separate on standing for some days are recrystallised from water and finally from alcohol. It crystallises in small yellow prismatic needles containing water of crystallisation, and when anhydrous melts at 147°. It is optically active, and whereas Leger found in ethyl acetate solution $[a]_D$ − 10·4, Jowett and Potter, who employed alcohol, found $[a]_D$ = − 8·3. Barbaloin is readily soluble in water and alcohol, and its alkaline solutions, which are orange coloured, possess a green fluorescence. The aqueous solution gives with basic lead acetate a deep yellow precipitate.

Diacetyl-barbaloin, $C_{21}H_{18}O_9(C_2H_3O)_2$ (Leger, Comptes rend., 1897, 125, 187), *dibenzoyl-barbaloin*, and *tetra-benzoyl-barbaloin* (Leger, Centralbl., 1903, 234) are amorphous. *Tetra-acetyl-barbaloin*?, $C_{24}H_{26}O_{11}$? (Groenewald, Tilden, Jowett and Potter, *loc. cit.*), yellow crystalline powder, melts at 95—96°. *Tribrom-barbaloin*, $C_{21}H_{17}O_9Br_3$, crystalline powder (L), $C_{16}H_{15}O_7Br_3$ (Groenewald, Jowett and Potter), has melting-point 191—192°, and gives the tetra-acetyl compound $C_{24}H_{23}O_{11}Br_3$?, yellow needles, melting-point 135°.

Tetrabrom-barbaloin, $C_{21}H_{16}O_9Br_4$, yellow needles, *tetrachlorbarbaloin*, $C_{21}H_{16}O_9Cl_4$, *penta-acetyl-tetrachlor-barbaloin*, $C_{21}H_{11}O_9Cl_4(C_2H_3O)_5$, leaflets, melting-point 166°, and *penta-benzoyl-tetrachlorbarbaloin*, $C_{21}H_{11}O_9Cl_4(C_7H_5O)_5$, yellow granules, have also been described (Leger). Barbaloin has been shown to occur in the *A. socrotina*, in Curaçoa aloes (Tschirch and Hoffbauer, Arch. Pharm., 1905, 243, 399), Jafferabad aloes, Uganda aloes (Leger, J. Pharm. Chim., 1907, 25, 476), and Leber? aloes. According to Tutin and Naunton (Pharm. J., 1914, 4, 37, 836) the main constituent of Curaçoa aloes is aloe-emodin.

ISO-BARBALOIN.—This compound, which is present in addition to barbaloin in Barbadoes aloes and is more soluble in solvents, possesses the formula $C_{21}H_{20}O_9$, crystallises from water with $3H_2O$, from methyl alcohol with $4H_2O$, and is isomeric with barbaloin. It is readily distinguished from this latter owing to the fact that with copper sulphate and sodium chloride in watery solution (Klunge's reaction) it gives a violet-red coloration (Leger, Comptes rend., 1900, 131, 55), which is deepened on addition of alcohol. It is optically active and in acetic ether solution has $[a]_D$ = − 19·4 (Leger, Chem. Centralblatt, 1903, 1, 235). When oxidised with sodium peroxide it gives *formic acid*,

d-arabinose (Leger, *loc. cit.*), and *aloe-emodin*, and according to this author is a glucoside of this latter containing the sugar nucleus attached to the hydroxyl in position 8.

Tetrachloroiso-barbaloin, $C_{21}H_{16}O_9Cl_4$, yellow needles, is converted by the action of sodium peroxide into the same tetrachlor-aloe-emodin as that given in this way by tetrachlor-barbaloin. *Tetrabromiso-barbaloin*, $C_{21}H_{16}O_9Br_4$, behaves similarly with production of tetrabrom-aloe-emodin (Leger, Comptes rend., 1902, 134, 1111). Finally, *dibenzoyliso-barbaloin*, $C_{21}H_{18}O_9(C_7H_5O)_2$, can be prepared by the action of benzoyl chloride in pyridine solution on iso-barbaloin.

NATALOINS.—Nataloin can be isolated (Leger, Comptes rend., 1899, 128, 1401) by digesting ground Natal aloes with cold acetone to remove resin, and then extracting the residue with boiling methylic alcohol. On cooling yellow crystals separate, and from these by fractional crystallisation from alcohol, nataloin can be separated from the less soluble homonataloin.

Nataloin forms pale yellow scales, soluble in alkaline solutions and ammonia, sparingly soluble in water and ether, but more readily so in ethyl acetate. It readily dissolves in concentrated hydrobromic and hydrochloric acids. *Homonataloin* crystallises in yellow laminæ, and both this and nataloin are distinguished from barbaloin by the fact that with sulphuric acid and either manganese dioxide or potassium bichromate, a green coloured liquid is produced, whereas with sodium carbonate and ammonium persulphate the solution of these aloins develops a violet tint. Homonataloin and nataloin are not isomeric as is the case with barbaloin and iso-barbaloin, and to these at first Leger assigned the respective formulæ $C_{15}H_{16}O_7$ and $C_{16}H_{18}O_7$.

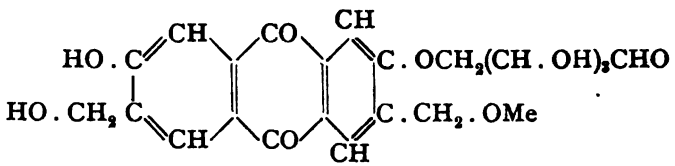
Tschirch and Klaveness (Arch. Pharm., 1901, 239, 231) could not prepare homonataloin from these aloes, but considered the formula $OMeC_{15}H_{10}O(OH)_5$ applicable to nataloin. The yellow amorphous penta-acetyl derivative melts at 125—126°, and the penta-benzoyl derivative at 168°. By the action of nitric acid, nataloin gives picric and oxalic acids.

When nataloin or homonataloin are treated with sodium peroxide (Leger, Comptes rend., 1902, 134, 1111), *methylnat-aloe-emodin* (a dihydroxy methoxymethyl-anthraquinone, $C_{16}H_{12}O_5$), orange-yellow needles, melting-point 238°, is produced, and this is soluble in alkalis with an orange, and in sulphuric acid with a violet coloration. Optically active pentoses are simultaneously obtained.

Both nataloin and homonataloin are optically active, the former having in ethyl acetate solution $[\alpha]_D$ – 107·7, and the latter $[\alpha]_D$ – 112·6 (Leger, *ibid.*, 1902, 134, 1584), and as a result of these obser-

vations, it was now suggested by this author that the probable formulæ of these compounds are respectively $C_{23}H_{26}O_{10}$ and $C_{22}H_{24}O_{10}$. In a later paper, Leger (J. Pharm. Chim., 1903, vii., 17, 13) finally adopted the formula $C_{23}H_{26}O_{10}$ for nataloin, and described its amorphous tetra-benzoyl and hexa-benzoyl compounds. Methylnatal emodin on distillation with zinc-dust gives methylanthracene, and at 170°, with hydrochloric acid, natalemodin. The latter consists of long orange-yellow needles melting at 220·5°, which dissolve in sulphuric acid with a red and in caustic soda solution with a violet coloration. Homonataloin (Comptes rend., 1912, 155, 172) yields on hydrolysis a *d*-arabinose, and nataloin in this way gives apparently the same sugar.

Leger in 1914 (Comptes rend., 158, 185) assigned the following constitution to homonataloin:—



and considered that nataloin may be similarly represented if the CH_2OH group in the above formula is replaced by CH_2CH_2OH.

When homonataloin and nataloin are heated with acetic anhydride for one hour at 105—110°, three isomeric penta-acetyl derivatives β, γ, and δ are obtained together (*ibid.*, 1189). *β-penta-acetyl-homonataloin* melts at 247°, and is inactive, whereas the γ-derivative melts at 199—200° and has $[a]_D$ − 54·2°. The δ compound is amorphous. *β-penta-acetyl-nataloin*, melting-point 245°, is also inactive, the γ compound, melting-point 198°, has $[a]_D$ − 53°, and the δ derivative $[a]_D$ − 56·1°.

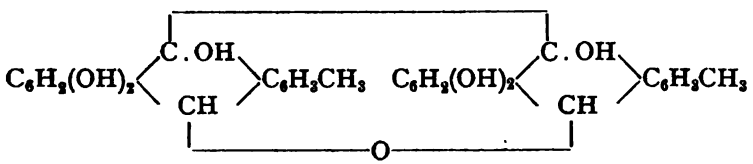
From these on hydrolysis β, γ, and δ aloins are obtained, and each compound on reacetylation at 105—110° yields again a mixture of these three isomeric acetyl compounds.

Goa Powder.

Goa powder, also known as araroba or crude chrysarobin, is a substance found in the trunk of the *Andira araroba*, a tree growing in Bahia, Brazil. It is scraped out of the cavities, and consists of an umber-brown powder, usually admixed with woody fragments, from which it is freed by sifting. It is employed in medicine in the form of an ointment for parasitic affections of the skin.

Goa powder was first examined in 1875 by Attfield (Pharm. J., (111), 5, 721), who considered it to consist largely of chrysophanic acid.

Liebermann and Seidler (Ber., 11, 1603) also detected the presence of chrysophanic acid in this drug, but showed that the main constituent is *chrysarobin* $C_{30}H_{26}O_7$, from which chrysophanic acid can be obtained by oxidation. Hesse (Annalen, 1899, 309, 32) as the result of his examination considered that chrysophanic acid is not present in Goa powder, but that the latter consists of two parts of chrysarobin $C_{15}H_{12}O_3$ and one part of chrysarobin methyl ether. Chrysarobin he found to be isomeric with chrysophan-hydranthrone, into which it was converted by the action of hydrochloric or hydriodic acids, but on acetylating this latter the reverse change takes place, triacetyl-chrysarobin being formed. Jowett and Potter (Chem. Soc. Trans., 1902, 81, 1575) considered, however, that chrysarobin and the chrysophan-hydranthrone of Liebermann and Seidler are identical, and that moreover the other constituents of Goa powder were *dichrysarobin* $C_{30}H_{24}O_7$, *dichrysarobin methyl ether* $C_{30}H_{22}O_7CH_3$, and a substance $C_{17}H_{14}O_4$. For dichrysarobin which yielded the same oxidation and reduction products as chrysarobin, the following constitution was suggested by these authors:—



Oesterle and Johann in 1910 (Arch. Pharm., 248, 476) obtained emodin methyl ether from chrysarobin, and suggested that the dichrysarobin of Jowett and Potter was not a pure compound.

Finally, Tutin and Clewer (Chem. Soc. Trans., 1912, 101, 290), by a very exhaustive examination of Goa powder, have determined the exact nature of the substances it contains. According to these authors, the commercial product is somewhat variable as to the relative proportion of the substances present, some samples being devoid of certain constituents which are present in others. Those invariably present, however, are *chrysophanic acid*, *emodin methyl ether*, the anthranols of these compounds, and the methyl ether of *dehydroemodinanthranol*, $C_{16}H_{12}O_4$. One sample, again, contained free emodin, and in two others a new compound, *ararobinol*, $C_{23}H_{16}O_6$, was found to exist. The chrysarobin of Jowett and Potter was a mixture of chrysophanol-anthranol and emodinanthranol, and their

dichrysarobin, of chrysophanol-anthranol and the monomethyl ether of dehydroemodinanthranol.

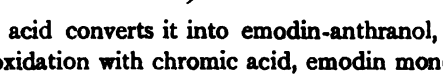
Ararobinol, $C_{22}H_{16}O_5$, crystallises in yellow flattened crystals which decompose about 225°, and possess no definite melting-point. It is insoluble in 1·5 per cent. aqueous potassium hydroxide, but dissolves in a 10 per cent. solution of the alkali to form a yellow liquid. Very characteristic is its reaction with sulphuric acid with which it at first acquires an orange colour. On shaking, the liquid gradually becomes blue and this subsequently passes through green, to a dull grey tint.

Oxidised with chromic acid, ararobinol gives chrysophanol, and when reduced with hydriodic acid *dihydro-ararobinol*, $C_{22}H_{18}O_5$, greenish-yellow plates, is produced. *Triacetyl-ararobinol*,

$$C_{22}H_{13}O_5(C_2H_3O)_3,$$

nearly colourless flattened prisms, decomposes at 225°.

Dehydro-emodinanthranol monomethyl ether, $C_{16}H_{12}O_4$, forms pale yellow needles, which melt and decompose at 265°. It oxidises with greater difficulty than the anthranols, and probably differs from the monomethyl ether of emodin-anthranol by two atoms of hydrogen. Its constitution, according to Tutin and Clewer, can be represented as follows:—



Hydriodic acid converts it into emodin-anthranol, melting-point 255°, and by oxidation with chromic acid, emodin monomethyl ether is produced.

ALKANET.

The Arabic name *Al-henneh*, modified to *alkanna* or *al-kenna*, was originally applied to the lythraceous shrub *Lawsonia alba* (Lam.), the root of which was described as *Radix Alkannæ vera*, in contradistinction to the root of our alkanna, which is *Anchusa tinctoria* (Lam.), and which became known as *Radix Alkannæ spuria tinctoria*. The latter, or *False alkanet*, is also known as *Orcanette*, Fr.; *Orkanet*, Ger.; Languedoc bugloss or dyers' bugloss, *Radix Alkannæ spuria*. A rough plant with downy spear-shaped leaves, and clusters of purplish or reddish flowers; belongs to the *Boraginaceæ*. Found in Asia Minor, Greece, Hungary, etc. The roots, which have an astringent taste, occur in commerce, varying from the thickness of a quill to that of a finger.

Alkanet is one of the more ancient dyestuffs, having been employed by the Romans, but, on the other hand, it does not appear

at any time to have attained such importance as madder, indigo, or even turmeric. The colouring matter of alkanet, known as *anchusin* or *alkannin*, has been examined by several chemists, but it is doubtful whether this compound has as yet been obtained in a chemically pure condition. Its composition is variously given as $C_{17}H_{10}O_4$ (Pelletier, Annalen, 6, 27), $C_{35}H_{20}O_8$ (Bolley and Wydlers, Annalen, 62, 41), $C_{15}H_{14}O_4$ (Carnelutti and Nasini, Ber., 13, 1514), and $C_{15}H_{14}O_4$ or $C_{15}H_{12}O_4$ (Liebermann and Römer, Ber., 20, 2428).

Alkannin forms a dark red amorphous powder possessing a beetle-green iridescence, is readily soluble in most of the usual solvents, and its alkaline solution is deep blue coloured. On distillation with zinc-dust it gives, according to Liebermann and Römer, both methyl anthracene and anthracene.

Diacetylalkannin, $C_{15}H_{12}O_4(C_2H_3O)_2$, forms a dull yellow micro-crystalline powder (C. and N.).

According to Eriksson (Ber. Deut. pharm. Ges., 1910, 20, 202), alkannin consists of two red pigments, the one being coloured green and the other blue by the action of alkalis. Red crystals have been observed by Tschirch in spaces in the cortex of old specimens of alkanet root. As alkannin is insoluble in water, in dyeing with alkanet an alcoholic extract is usually employed; and with aluminium and iron mordanted fabrics, violet and grey shades are respectively produced. These colours, however, are not fast to light, and are somewhat readily affected by weak alkalis or acids.

Haussmann of Mulhouse introduced alkanet into calico-printing, and for a short time it appears to have played a quite important part, but it is now little if at all employed in Europe for ordinary dyeing purposes. It is still used for colouring artificial wines, pomades, hair-oils, sweets, etc., and for these purposes it is well adapted on account of its ready solubility and harmless nature.

Böttger (J. f. prakt. Chem., 107, 146) and Eng (Jahres., 70, 935) recommend the use of papers stained by alkanet as indicators in alkalimetry.

According to Jolin (Chem. Schriften über Alkanna, iv., 84), Thomson (Pharm. J., [3], 16, 860), and Eriksson (*loc. cit.*), alkanet root contains from 5—6 per cent. of anchusin.

ONOSMA ECHOIDES.

Onosma echoides is a biennial plant frequent throughout the Western Himalaya from Kashmir to Kumaon. It is widely distributed from Siberia and Carbut to France (Watt's "Dictionary of Economic Products of India," 1891, 5, 487). The roots are

violet coloured and yield a dye which is readily extracted by alcohol, giving a red solution, but this is very sparingly soluble in water. In various districts of India it is employed for dyeing wool, and on account of its solubility in oils and fats, to which it imparts a red colour, is also used as a substitute for alkanet. According to Watt (*loc. cit.*) the bruised root is employed medicinally as also are the leaves and flowers of this plant.

The general properties and colour reactions of the dye present in the root are very similar to those given by alkanet, and there can be little doubt that it contains either the same or closely allied colouring matters (Perkin, private communication).

VENTILAGO MADRASPATANA (Gaertn.)

is a large climbing shrub belonging to the order *Rhamnaceæ*, the root-bark of which furnishes a dyestuff much valued in Southern India. It is very common in the Western Peninsula from the Konkan southwards, as well as in Ceylon and Burma, and, according to Lostard, it is collected in Mysore at certain periods of the year and exported to other districts of India.

The following are a few of its vernacular names: pitti (*Hindi*); raktapita (*Bengali*); pappili-chakka, surralpattai (*Tamil*); popli-chukai (*Kan*); lokandi, kanwail (*Bomb*).

The root-bark appears as dark purplish-brown scales, ribbons, or filaments, the dust from which, when it is ground to powder, irritates the throat in a marked manner. When treated with boiling water or alcohol it gives a red solution, which on addition of caustic alkali, changes to a deep crimson.

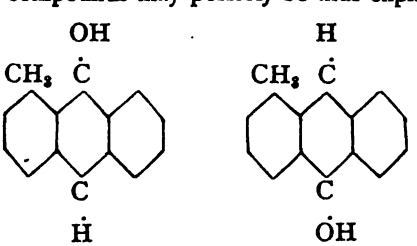
Perkin and Hummel (Chem. Soc. Trans., 1894, 65, 923), who examined this dyestuff, extracted the root-bark with carbon disulphide, and obtained in this manner a resinous colouring matter, *ventilagin*, together with the crystalline non-tinctorial substances described below.

Ventilagin, $C_{15}H_{14}O_6$, consists of a reddish-brown brittle resin which, when distilled with zinc-dust, gives *a*-methyl anthracene, and when treated with zinc-dust in alkaline solution behaves as a derivative of *methyl anthraquinone*. Dilute alkalis dissolve it with a purple-violet coloration, and the corresponding salts are obtained as violet precipitates on adding sodium or potassium chlorides to these solutions. According to Perkin and Hummel, ventilagin is possibly allied to alkannin $C_{15}H_{14}O_4$, the colouring matter of alkanet, *Anchusa tinctoria* (Lam.), and may differ from this merely by the possession of two additional hydroxyl groups.

Emodin monomethyl ether, $C_{16}H_{12}O_5$, melting-point 200°, consists of orange-red needles, and is identical with that subsequently isolated from the root of the *Polygonum cuspidatum* (Sieb. and Zucc.) (Perkin, Chem. Soc. Trans., 1895, 67, 1084). A similar, if not identical, substance was isolated by Schwabe (Arch. Pharm., 1888, 26, 569), and by Thorpe and Miller (Chem. Soc. Trans., 1892, 64, 6) from the bark of the *Rhamnus frangula* (Linn.), and it is also present in rhubarb and the *Rumex ecklonianus* (*loc. cit.*) and Goa powder.

Trihydroxy-a-methyl anthranol-monomethyl ether (A), $C_{16}H_{14}O_4$, colourless needles, decomposes about 260° before melting, and is soluble in alkaline solutions with a yellowish-brown coloration. On gentle oxidation with chromic acid it is converted into emodin methyl ether, melting-point 200° (*loc. cit.*), and the same reaction takes place when its alkaline solution is oxidised with hydrogen peroxide. It closely resembles the dehydro-emodin anthranol monomethyl ether, subsequently isolated from Goa powder by Tutin and Clewer (Chem. Soc. Trans., 1912, 101, 290).

Trihydroxy-a-methyl anthranol-monomethyl ether (B), $C_{16}H_{14}O_4$, pale yellow needles, melting-point 173°, when oxidised with chromic acid is also converted into the emodin methyl ether, melting-point 200°. As two methyl anthranols are capable of existence, the isomerism of these compounds may possibly be thus explained:—



Substance $C_{16}H_8O_8$, orange-red crystalline powder, melting-point 275—280°, is soluble in alkaline solutions with an orange-red coloration, and when heated with zinc-dust gives a hydrocarbon which resembles *a*-methyl anthracene.

Substance $C_{17}H_{12}O_5$? is a chocolate, crystalline powder, soluble in dilute alkali with a yellow coloration, and this solution, on exposure to air, deposits a blue amorphous precipitate.

Dyeing Properties.—On striped printed calico the root-bark gives with alumina mordant a claret-red, not unlike that of alizarin bordeaux; with iron mordant a greyish-lilac, which in strong colours approaches a black; and with a mixture of the two a very purplish dark chocolate. The colours are moderately fast to soap, although

considerably behind the alizarin colours in this respect. On oil-prepared calico ventilago gives with alumina mordant a rich claret brown, with chromium mordant a very black purple, and with iron mordant a good purplish-black shade. On wool chromium mordant gives a good purplish-brown, alumina a bordeaux red, tin a brighter red similar to an alizarin red with alumina mordant, and iron mordant gives dark dull purple and black. On silk similar colours are produced. No difficulty is experienced in dyeing with ventilago, and no additions to the dye-bath are necessary, except in the case of wool, with which it is desirable to add calcium acetate in order to correct the strong acidity of the mordanted fibre. Owing to the slight solubility of the colouring matter in water, the dyeing does not commence until the temperature reaches 70—80°. The root-bark appears to contain from 8—10 per cent. of ventilagin.

COCHINEAL.

This important natural dyestuff, which, in its native country, Mexico, was used as a dye and cultivated by artificial means at a remote period of history, was for a long time considered to be of vegetable origin. Cochineal, however, consists of the dried body of an insect, the *Coccus cacti*, which lives upon a species of cactus (the *Nopalea coccinellifera* (S.-Dyck) or *Nopal*), a plant which is found in the wild condition, but which, for the sake of the insect, is cultivated in gardens which are termed *Nopaleries*. The collection of the insects takes place before the commencement of the rainy season, and they are then brushed either into straw baskets or into basins of tinned iron. A number of insects are left upon each plant, and a new generation is produced, which is again gathered at a suitable period. The insects are killed by immersion in boiling water, or are enclosed in a linen bag and placed in an oven; by the latter process the peculiar white down covering the insect is preserved, but in the former case is lost.

In Mexico and Central America two varieties of cochineal are known—the home-grown, or fine cochineal (*grana fina*), and the wild, or forest cochineal (*grana silvestra*). The former is more valuable than the latter, and is richer in colouring matter. Since 1830 the cultivation of cochineal was introduced into Spain and the Canary Islands, Algeria, and Java, but the most productive of these newer plantations were those of Java. Since the discovery of the coal-tar colours, the consumption of cochineal as a dye-stuff has gradually decreased, and at the present time it is only employed in a

minor degree. According to Liebermann, cochineal contains about 10 per cent. of colouring matter (Ber., 18, 19).

Carminic acid, the colouring matter of cochineal, was first isolated by Pelletier and Caventou (Ann. Chim. Phys., (2), 8, 250), and was subsequently examined by Preisser (Annalen, 52, 375; J. Pharm. Chim., (3), 5, 191) and Arppe (Annalen, 55, 101); but Warren de la Rue (*ibid.*, 64, 1) was the first to isolate this substance in a pure condition, and described it as a purple-brown mass, which, on grinding, yields a bright-red powder, easily soluble in water and alcohol, but not in ether. The mean of his analyses gave 54·13 per cent. of carbon, 4·62 per cent. of hydrogen, and 41·25 per cent. of oxygen (by difference), and from these figures he deduced the formula $C_{14}H_7O_8$ or $(C_{14}H_7O_8)_2$.

Schützenberger (Ann. Chim. Phys., (3), 54, 52), on the other hand, was the first chemist who succeeded in obtaining carminic acid in a crystalline condition. He precipitated the colouring matter, from an aqueous cochineal extract, in the form of its lead compound, suspended this in water, and decomposed it with sulphuretted hydrogen. The carminic acid thus liberated dissolved in the water and was recovered from this solution by evaporation at a low temperature. The product, dissolved in alcohol, was treated with ether to precipitate certain impurities, and the liquid partially evaporated, when, on cooling, a crystalline mass was obtained, which Schützenberger considered to consist of two substances, carminic acid, $C_9H_8O_5$, and oxycarminic acid, $C_9H_8O_6$, the latter being distinguished by its solubility in ether.

Schaller (J., 1864, 410), who prepared carminic acid by the same method, assigned to it, however, the formula $C_9H_8O_6$.

The work of Hlasiwetz and Grabowski (Annalen, 141, 329) indicated that carminic acid was a glucoside which could be decomposed into a sugar and a new colouring matter, *carmine red*:—

$$\underset{\text{Carminic acid.}}{C_{17}H_{18}O_{10}} + 2H_2O = \underset{\text{Carmine red.}}{C_{11}H_{12}O_7} + \underset{\text{Sugar.}}{C_6H_{10}O_5}$$

but according to Liebermann (Ber., 18, 1969; Will and Leymann, *ibid.*, 18, 318; and Von Miller and Rohde, *ibid.*, 26, 2647), this is incorrect.

Coccinin, according to Hlasiwetz and Grabowski, is produced when carminic acid is fused with caustic potash. It crystallises from alcohol in straw-yellow needles or leaflets, dissolves in alkalis with a yellow colour, which, by air oxidation, develops first a green, then violet, and, finally, a purple tint. The analyses of this substance were in agreement with the formula $C_{14}H_{12}O_5$.

Ruficoccin.—By heating carminic acid with sulphuric acid to 130—140° C., Liebermann and van Dorp (Annalen, 163, 105) obtained a new colouring matter ruficoccin, $C_{16}H_{10}O_6$, and this consisted of a bright-red powder, sparingly soluble in hot water and ether, with a greenish-yellow fluorescence. On distillation with zinc-dust, it yielded a colourless crystalline hydrocarbon, $C_{16}H_{12}$, melting-point 183—188° C., from which, by oxidation, a quinone melting at 250° C. could be produced.

Fürth, somewhat later (Ber., 16, 2169), prepared the same hydrocarbon by the distillation of both cochineal carmine and coccinin with zinc-dust.

Ruficarmine, $C_{16}H_{12}O_6$, can be obtained, according to Liebermann and van Dorp, by heating carminic acid with water in a sealed tube at 200° C. It consists of a carmine-red powder, easily soluble in alcohol.

In view of the uncertainty existing as to the percentage composition of carminic acid, Schunck and Marschlewski (Ber., 27, 2980) submitted this substance to an elaborate process of purification, and, using in their operations as low a temperature as possible, obtained a product which crystallised from alcohol in red prismatic needles. Their analyses agreed closely with that required by the formula $C_{11}H_{12}O_6$, and the percentage composition approximately with the figures given by Warren de la Rue, and also by Schützenberger.

On the other hand, analyses by Miller and Rohde (Ber., 30, 1762) pointed to the formula $C_{12}H_{11}O_7$ or $(C_{12}H_{11}O_7)_2$, but according to the more recent work of Liebermann, Höring and Wiedermann (Ber., 1900, 33, 149), it now appears that the correct formula for carminic acid is $C_{22}H_{22}O_{13}$.

The most simple method of purification of carminic acid is that devised by Miller and Rohde. A solution of the crude colouring matter in five times its weight of water is diluted with four times its volume of acetic acid. The filtered liquid, on standing over sulphuric acid, gradually deposits the carminic acid in a crystalline condition.

Carminic acid crystallises in red prisms, easily soluble in water and alcohol, with a purple-red colour. It possesses no melting-point, but darkens at 130°, and at 250° becomes quite black.

By the action of alcoholic potassium acetate, carminic acid (Perkin and Wilson, Chem. Soc. Trans., 1903, 83, 139) yields two potassium salts, viz. :—

Monopotassium carminate, $C_{22}H_{21}O_{13}K$, which is red coloured; and

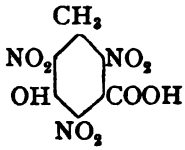
Dipotassium carminate, $C_{22}H_{20}O_{13}K_2$, soluble in water with a violet-red coloration.

Hexabenzoylcarminic acid, $C_{22}H_{16}O_{13}(C_7H_5O)_6$, obtained by digesting carminic acid with benzoyl chloride (Liebermann, Höring and Wiedermann), is an orange-coloured powder, easily soluble in benzene.

Octacetylcarminic acid, $C_{22}H_{14}O_{13}(C_2H_3O)_8$, crystallises in golden-yellow needles, melting-point 155—165°, and is readily prepared by the action of acetic anhydride in presence of zinc chloride or sulphuric acid on carminic acid (Miller and Rohde).

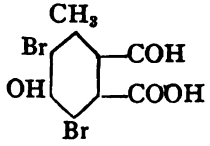
THE CONSTITUTION OF CARMINIC ACID.

Nitrococcussic acid was obtained by W. de la Rue from carminic acid by the prolonged action of boiling nitric acid. It was subsequently studied by v. Kostanecki and Niementowski (Ber., 18, 250), and was found to be identical with the *trinitrocresotinic acid*, of the following constitution :—

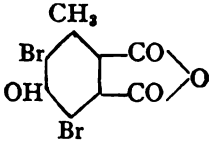


When carminic acid dissolved in 50 per cent. acetic acid is treated with an excess of bromine, and the solution digested at the boiling heat, two substances, known as α- and β-bromcarmines, are produced (Will and Leymann, Ber., 18, 3180).

α-Bromcarmine, $C_{10}H_4Br_4O_3$, the more sparingly soluble substance, crystallises in colourless needles, and melts at 247—248°, with decomposition. When oxidised with potassium permanganate in alkaline solution, it gives *dibrommethylhydroxyaldehydrobenzoic acid*—

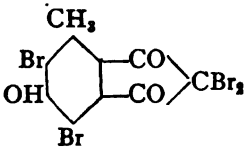


and *dibrommethylhydroxyphthalic anhydride*—

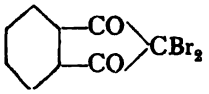


On treatment with hot caustic soda solution, α-bromcarmine yields, in addition to a purple-red colouring matter, dibrommethylhydroxyphthalic acid, and *bromoform* (Miller and Rohde). As a result of

this reaction, these authors assigned to α-bromcarmine the constitution of a *methylhydroxytetrabromdiketohydrindene*—

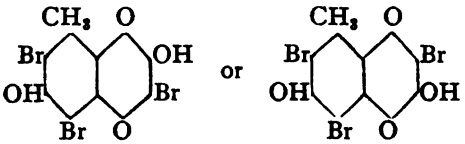


for Zincke (Ber., 20, 3227; 21, 2388) had previously shown that dibromdiketohydrindene itself—

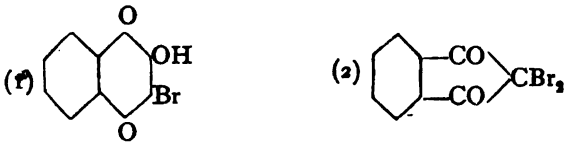


under similar treatment yields both phthalic acid and bromoform.

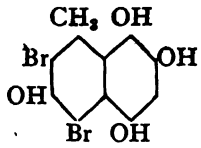
β-Bromcarmine, $C_{11}H_6Br_2O_4$, is obtained as a yellow amorphous powder, easily soluble in alcohol (Will and Leymann), and is best purified by means of its potassium salt. Crystallised from acetone, it separates in orange needles, melting at 232° (Will and Leymann) or 288° (Miller and Rohde). By the action of bromine in the presence of 50 per cent. acetic acid solution, it is converted into α-bromcarmine. As a result of their investigation, Miller and Rohde ascribed to β-bromcarmine the constitution of a *methyldihydroxytribrom-a-naphthaquinone*, possessing one of the following formulæ :—



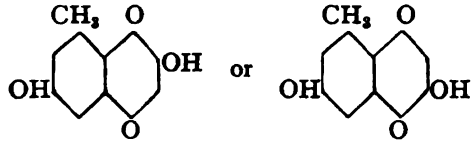
This suggestion was supported by the fact that bromoxynaphthaquinone (1), on treatment with bromine and caustic soda solution, is converted into dibromdiketohydrindene (2) (Zincke, *loc. cit.*)—



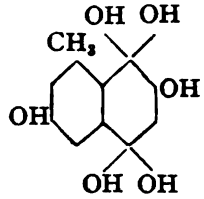
Additional support for this view was obtained by a study of the behaviour of β-bromcarmine with zinc-dust in alcoholic solution. Thus the acetyl compound of the reduction product, melting-point 206°, gave, on analysis, numbers agreeing with those of the acetyl derivative of a *methyldibromdihydroxynaphthahydroquinone*, possessing the following formula :—



From a consideration of the points above enumerated, Miller and Rohde considered that the constitution of carminic acid could be represented by one or other of the following expressions :—



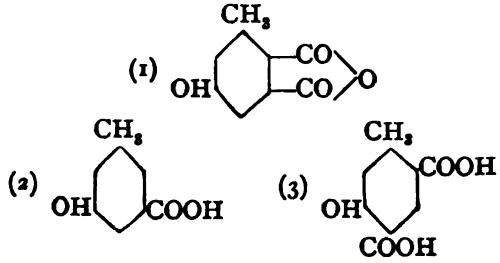
As, however, such formulæ require C = 64·7 per cent., H = 3·92 per cent., figures which are much higher than those given by the analysis of carminic acid itself, these authors suggested the addition of two molecules of water of hydration, as shown below :—



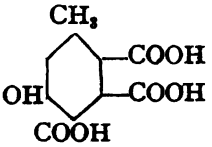
A substance of this constitution would require C = 55 per cent., and H = 5 per cent.

Somewhat later, Liebermann and Voswinkel (Ber., 30, 688) studied the oxidation of carminic acid with alkaline potassium permanganate at the ordinary temperature, and in this way succeeded in producing two important acids.

Cochenillic acid, $C_{10}H_8O_7$, crystallises in colourless needles, which melt at 224—225° with evolution of CO_2. It is tribasic, and at 260° is converted into *hydroxymethylphthalic anhydride* (1). When heated with water in a sealed tube at 210° it yields symmetrical *cresotinic acid* (2)—

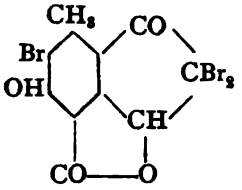


and in the same manner at a lower temperature, 170°, gives *α-coccinic acid* or *m-hydroxyuvitic acid* (3). The constitution of cochenillic acid is therefore as follows :—

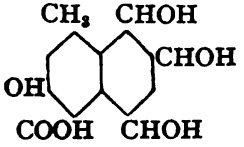


α-Coccinic acid, $C_9H_8O_5$, the second product of the oxidation, which, as already indicated, can also be prepared from cochenillic acid, proved to be identical with the hydroxyuvitinic acid of Oppenheim and Pfaff (Ber., 7, 929). It consists of colourless needles, melting-point 239°.

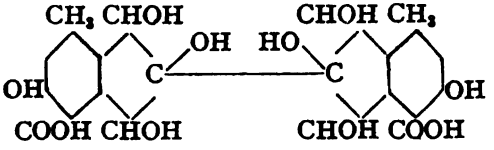
Liebermann (*ibid.*, 30, 1731), whilst agreeing with the diketohydrindene constitution which had been assigned to α-bromcarmine by Miller and Rohde, considered that β-bromcarmine was an indone rather than a naphthoquinone derivative, and could be better represented as follows :—



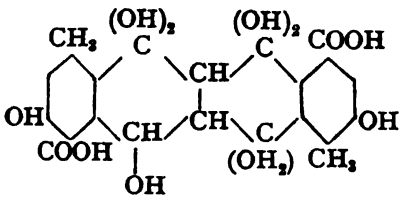
It was probable, indeed, that carminic acid itself was a hydrindene or bishydrindene derivative, and the following constitutions were at the time suggested for it :—



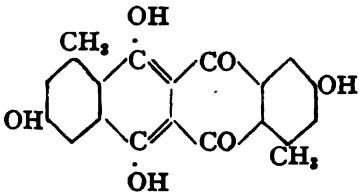
or



In a subsequent paper, however, Liebermann and Voswinkel (Ber., 37, 3344) consider that carminic acid is possibly a *tetrahydrate of α-dimethyldihydroxynaphthacenequinonedicarboxylic acid*—

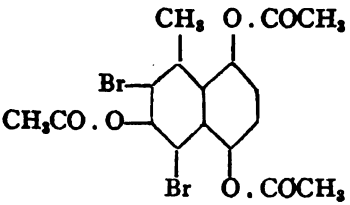


and it was observed that the dimethyltetrahydroxynaphthacene-quinone—



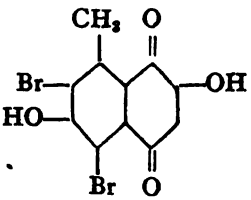
prepared by these authors not only possessed weak tinctorial property of a cochineal-like character, but in several respects closely resembled carminic acid itself.

Rohde and Dorfmüller (Ber., 1910, 33, 1363) further examined β-bromo-carmine, and obtained results which support the naphthoquinone constitution assigned to it by Miller and Rohde (*loc. cit.*), but disprove Liebermann's contention that it is a derivative of indone. By reduction with zinc-dust and acetic acid and subsequent acetylation, β-bromo-carmine gives the compound $C_{17}H_{14}O_6Br_2$:—



colourless needles, melting-point 208° C.

Simultaneous hydrolysis and oxidation converts this into the substance

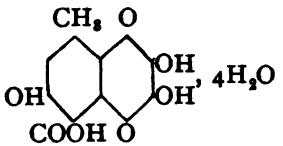


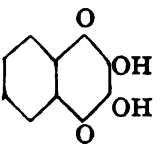
orange prisms, melting-point 258° C.; and it thus appears that

by the latter treatment an hydroxyl has entered the quinone nucleus. The diacetyl derivative melts at 233° C. When distilled with zinc-dust, this product, and also β-bromo-carmine itself, give naphthalene.

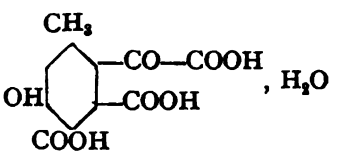
A valuable contribution to the subject was made by Dimroth (Ber., 1909, 42, 1611), who studied the oxidation of carminic acid with potassium permanganate at 0° in presence of sulphuric acid. The solution thus obtained gave nothing to ether, but on heating for three-quarters of an hour at 90°, it evolved carbon dioxide, and ether then extracted carminazarin.

Carminazarin crystallises from water in garnet-red needles, decomposing at 240—250°. It possesses the constitution (1), and is very similar to *iso*naphthazarin (2)—

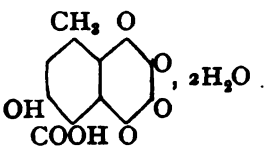
(1) 

(2) 

Its alkaline solution when treated with a stream of oxygen, is quickly decolorised with formation of 5 : 6-*dicarboxy*-4-*hydroxy*-*o*-*tolylglyoxylic acid*—



A further point of resemblance of carminazarine to *iso*naphthazarine is shown by its behaviour with nitric acid in glacial acetic acid, for whereas the latter gives tetraketotetrahydronapthalene, the former yields the analogous *Carminazarinquinone* crystallising in colourless prisms—

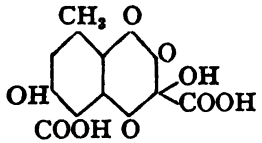


and which, when heated with water or acetic acid, passes back to carminazarin.

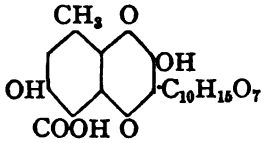
The intermediate product formed by the oxidation of carminic acid with permanganate at 0° insoluble in ether, and which, on heating, is transformed into carminazarin, is termed by Dimroth

carminoquinone. The constitutions assigned to this substance (1) and tentatively to carminic acid (2) are given below :—

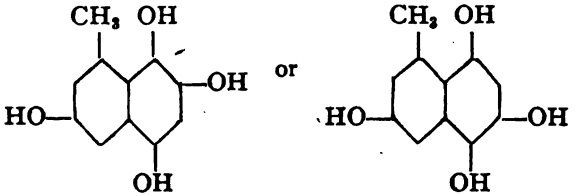
(1)



(2)



Carminic acid was, therefore, not a symmetrical compound, and the nature of the group $C_{10}H_{15}O_7$ was not then determined. At the time, Dimroth considered that the ***coccinin*** (see above) of Hlasiwetz and Grabowski, and which is prepared by fusing carminic acid with potassium hydrate, had probably the constitution of a ***tetrahydroxymethylnaphthalene***—



Later, Dimroth (Annalen, 1913, 399, 1) re-examined this product in detail, preparing it by fusing carminic acid with caustic potash at 170—200° C. To it he gave the formula $C_{17}H_{14}O_6$, and described the pale yellow crystalline ***tetra-acetyl derivative***, $C_{17}H_{10}O_6(CH_3CO)_4$, melting-point 242—244° C.

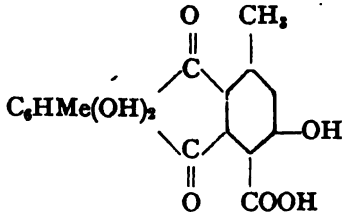
When coccinin was oxidised by means of air, or oxygen, in alkaline solution (6 per cent. NaOH), the colour changes above described occurred, and when the pure violet colour had been obtained, acidification with hydrochloric acid yielded a substance ***coccinone***, $C_{17}H_{12}O_7$, which forms dark brown glistening crystals and decomposes at 250° C. ; it yields a ***tri-acetyl derivative***,

$$C_{17}H_9O_7(CH_3CO)_3,$$

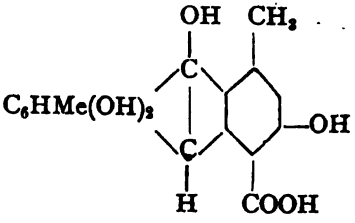
orange-red crystals, melting-point 210° C., and also forms three different barium salts (one of which has a composition analogous to the sodium hydrogen salt of 2 : 6-dihydroxy-8-methyl-*a*-naphthoquinone-3 : 5-dicarboxylic acid). Coccinone is reconverted into coccinin by reduction with zinc-dust and ammonia; on the other hand, alkaline oxidation by means of hydrogen peroxide below 20° C. gives rise to two products, (i) cochenillic acid, and (ii) an unexamined acid.

Dimroth now formed the opinion that coccinin and coccinone are derivatives of anthranol and anthraquinone respectively, and the

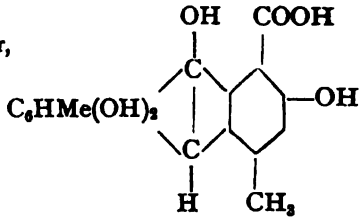
position of one of the hydroxy, methyl, and carboxyl groups in coccinone is made clear by the production from it of cochenillic acid. To coccinone Dimroth ascribes the structure—



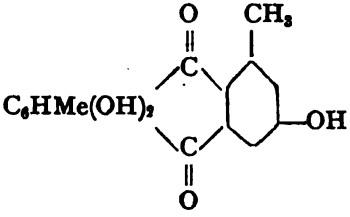
and to coccinin either the structure—



or,



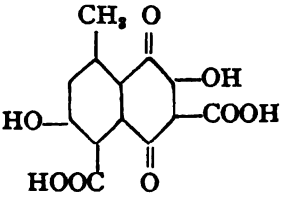
When heated with water at 200°—or dilute sulphuric acid at 170° C.—coccinone loses carbon dioxide, yielding *decarboxy-coccinone*, to which the structure—



is given; it forms red-brown crystals, and dissolves in alkalis to form purple-red solutions, and in concentrated sulphuric acid with a blue colour which becomes violet on addition of boric acid.

Not only coccinin, but carminic acid itself, has been further examined by Dimroth (*loc. cit.*), and as a result he considers that this substance is also a derivative of anthraquinone. He has oxidised carminic acid by means of hydrogen peroxide in aqueous caustic soda, using cobalt sulphate as catalyst, and in this way obtained in the first instance carminoquinone, but the reaction proceeded further with the formation, after acidification with 80 per cent. acetic acid, of a yellow crystalline compound, $C_{26}H_{12}O_{16}Na_2$, $5H_2O$, which, when triturated at 0° C. with dilute hydrochloric acid, yielded 2 : 6-*dihydroxy*-8-*methyl*-α-*naphthoquinone*-3 : 5-*dicar-*

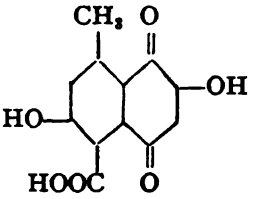
boxylic acid: pale yellow, hygroscopic crystals—



trisodium salt, $C_{12}H_5O_8Na_3$, $4H_2O$, orange needles.

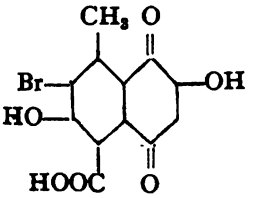
The orientation of this acid has been established by Dimroth by comparison of its colour reactions with those of 2 : 6-*dihydroxy-α-naphthoquinone*, synthetically prepared by Dimroth and Kerkovius, as also by its conversion into carminazarin by treatment with acid permanganate. Moreover, the structure previously assigned by Dimroth to carminazarin, viz. 2 : 3 : 6-trihydroxy-8-methyl-α-naphthoquinone-5-carboxylic acid, has been supported by conversion of carminazarin-quinone—the oxidation product of carminazarin—into a *diphenazin*, $C_{24}H_{14}O_2N_4$, by treatment with an alcoholic solution of *o*-phenylene-diamine. The product crystallises in yellow needles, and yields an *acetyl derivative*, $C_{28}H_{16}O_4N_4$.

When 2 : 6-dihydroxy-8-methyl-α-naphthoquinone-3 : 5-dicarboxylic acid—the oxidation product of carminic acid referred to above—is warmed with water, carbon-dioxide is eliminated with the production of 2 : 6-*dihydroxy*-8-*methyl*-α-*naphthoquinone*-5-*carboxylic acid*: brown-yellow needles—

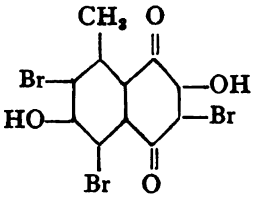


potassium salt, $C_{12}H_7O_6K$, lemon-yellow crystals; *dipotassium derivative*, $C_{12}H_6O_6K_2$, orange-red crystals.

This compound when brominated in glacial acetic acid at 40° yields a *monobrom derivative*, yellow needles, melting-point 240—244°,



which on treatment with hydrobromic acid yields *α-bromo-carmin*, whilst with bromine in cold methyl alcohol, the product is β-bromo-carmin (Will and Leymann), which proves that this body has the structure

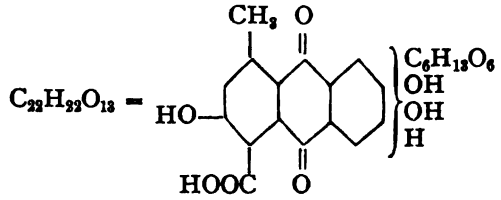


assigned to it by Miller and Rohde.

Beyond the above-mentioned decomposition products of carminic acid, Dimroth has obtained a 5 per cent. yield of hydrocarbons of the anthracene series by distillation with zinc-dust in an atmosphere of hydrogen. After oxidation of the mixture of hydrocarbons he isolated anthraquinone, and possibly α-methyl-anthraquinone.

By treatment of carminic acid with boiling dilute sulphuric acid, Dimroth has also obtained a 10 per cent. yield of trihydroxy-methyl-anthraquinone carboxylic acid ($C_{16}H_{10}O_7$), needles, melting-point above 300°, and this acid when heated with water at 230—240°, passes into trihydroxy-methyl-anthraquinone by loss of carbon dioxide.

Dimroth considered the possibility that the anthraquinone nucleus is produced during the reactions described above, but concluded that this is not the case, and that it is present as such both in carminic acid and coccinin. Dimroth formulates carminic acid thus—



On the other hand, C. and H. Liebermann (Ber., 1914, 47, 1213) bring forward arguments, chiefly the smallness of the yield of anthraquinone or anthracene derivatives obtained by Dimroth, in favour of the view that the anthracene nucleus is formed during the degradation reactions.

These authors have also re-examined the "ruficoccin" of Liebermann and van Dorp (see above), and conclude that it consists of a mixture of trihydroxy-methyl-anthraquinone carboxylic acid, and trihydroxy-methyl-anthraquinone, which is confirmation of the work of Dimroth. Incidentally they described *carminic anhydride*, $C_{22}H_{20}O_{12}$,

prepared by heating carminic acid with thionyl chloride—vivid red powder, resembling carminic acid, though less soluble. It is reconverted into the latter by the action of aqueous alkalis.

Technical Preparations of Cochineal.

Ammoniacal Cochineal.—When a solution of carminic acid in ammonia is allowed to stand for some time, there is formed a new compound, which appears to consist of carminic acid in which one of the hydroxyls has been replaced by an amino group. The formula assigned to this substance by Schützenberger was $C_9H_9NO_4$. This reaction, long known, has been utilised for the production of a new colouring matter termed *ammoniacal cochineal*, or *carminamide*, and this comes into commerce either as cakes or in the form of a paste.

The first variety is usually prepared by allowing one part of cochineal to stand in a closed vessel for three months with three parts of ammonia. The clear liquid is decanted, treated with about half its weight of gelatinous alumina, evaporated, and when the mass has become thick, it is cut up into cakes and dried.

The paste is manufactured in a somewhat similar manner, the ammonia, however, being only allowed to react for eight days. The clear liquid is then evaporated to about one-third its bulk without addition of alumina (Crookes, "Dyeing and Calico Printing").

Ammoniacal cochineal dyes much bluer shades than cochineal itself, and it is sometimes employed in conjunction with the latter. Its use is now very limited, but it finds some application in the blueing of bleached cotton.

Dyeing Properties of Cochineal.

Cochineal has been little employed in cotton dyeing, but was very largely used in silk and wool dyeing. It has now been practically replaced by the azo-scarlets.

Two shades of red are obtained upon wool with cochineal, namely, *crimson*, which is produced by means of aluminium sulphate, and a very fiery *scarlet*, for which stannous and sometimes stannic chlorides are employed.

For crimson, wool is mordanted with aluminium sulphate and tartar, and is then dyed in a separate bath with cochineal. The employment of calcium salts in the dyeing operation is not beneficial. Fairly good shades of crimson can also be obtained by mordanting and dyeing in a single bath with aluminium sulphate, oxalic acid, and cochineal. For scarlet, wool can be mordanted with stannous

chloride and tartar, and dyed in a separate bath with cochineal. A single-bath method, employing stannous chloride, oxalic acid, and cochineal, has, however, been very largely used for this purpose. On the other hand, preparations of stannic chloride, known as "tin spirits," "scarlet spirits," and "nitrate of tin," are and have been much employed by dyers of cochineal scarlet. Though, when used alone, stannic chloride does not give such brilliant shades as the stannous mordant, a mixture of both is considered to be beneficial. For very yellow shades of scarlet, yellow colouring matters can be added to the cochineal dye-bath, and of these "flavine" has been considerably employed.

Cochineal red on wool possesses considerable fastness to light, but has the defect that weak alkalis and soap cause it to acquire a duller or more bluish shade.

Wool mordanted with potassium dichromate gives with cochineal a good purple colour, whereas with ferrous sulphate and tartar, purplish, slate, or lilac colours can be produced. These mordants, however, are not employed in practice. A good crimson shade is produced by mordanting silk with alum, and dyeing with an extract of cochineal. In scarlet dyeing, silk is preferably first dyed yellow, then mordanted with "nitromuriate of tin," and finally dyed in a second bath with the assistance of cream of tartar. Silk can also be dyed in a single bath with cochineal, stannous chloride, and oxalic acid.

Lac Dye.

Lac dye is produced by an insect, the *Coccus lacca* or *ficus*, living on the twigs of various kinds of trees, particularly the *Ficus religiosa* (Linn.), the *Zizyphus jujuba* (Lam.), and the *Butea frondosa* (Roxb.). These insects appear usually in November, and subsequently fasten themselves to the fleshy portions of the young branches. Gradually the abdomen of the insects becomes covered by a viscous fluid, which slowly forms a cellule surrounding the animal. The substance composing this cellule is the *stick lac*. The cellule attains its full size in March, and the insect then exhibits the appearance of a red oval-shaped, smoothly polished lifeless sack entirely filled with a beautiful red liquid; its size is then the same as that of the fully grown cochineal (Crookes, "Dyeing and Calico Printing," p. 354). Commercial stick lac is chiefly gathered on the hilly banks of the Ganges in India, that for dyeing purposes possessing a deep red colour, whereas the pale perforated kind in which no insects exist is employed for varnish-making, and constitutes the material for *shellac*.

Of *lac*, the following varieties occur: *stick lac*, the crude product together with the twigs upon which it is formed: *grained lac*, the material removed from the twigs; and *caked lac*, the latter variety fused and cast into moulds.

Such a resinous material is not suitable for dyeing purposes, and a simple process is adopted to remove the colouring matter from the resin, or at least to obtain it in a more concentrated form. This consists in extracting the stick lac with hot dilute sodium carbonate solution, evaporating the extract, and moulding the residue into square cakes. According to Crookes (*loc. cit.*) the product, which is *lac dye*, contains on an average about 50 per cent. of colouring matter, 25 per cent. of resin, and 22 per cent. of earthy impurities.

Lac dye is an extremely ancient dyestuff, and was employed in the East for many centuries before it was known in Europe. It appears to have been introduced into this country about 1790. Early in the last century, lac dye was a very important article of commerce, so much so that at one time shellac was practically a bye-product of its manufacture. The position of these products has now been reversed, for whereas the dyestuff is almost defunct, the shellac industry is of considerable importance.

According to the older writers, the colouring matter of lac dye was considered to be identical with that of cochineal, but that this is not the case has been clearly indicated by Schmidt (Ber., 20, 1285).

Laccaic Acid.—Finely powdered lac dye, after treatment with dilute hydrochloric acid to remove mineral matter, is extracted with boiling water, and the colouring matter is precipitated from the resulting solution by means of lead acetate. The lead precipitate, suspended in water, is decomposed with sulphuretted hydrogen, and the filtrate which contains the free colouring matter is evaporated to dryness. The residue thus obtained is extracted with alcohol and ether is then added to the solution until a precipitate no longer forms. The filtered liquid on gradual evaporation deposits crystals of laccaic acid. According to Schmidt, the amount of pure colouring matter which can be isolated by this method from a kilogram of lac dye is 20 grams.

A simpler process has been described by Dimroth and Goldschmidt (Annalen, 1913, 399, 62), in which the stick lac is digested in water at 50° C., the clear red solution, after cooling, acidified with acetic acid, separated from the resinous matter that is precipitated, and, after evaporation to small bulk, acidified with hydrochloric acid. When the crude product thus obtained is crystallised from hot 85 per cent. formic acid, washed, dried (at 60—70° C.), and recrys-

tallised from hot dilute hydrochloric acid, laccaic acid separates in the form of dark red microscopic rhombohedra. The acid is soluble in water yielding blood-red solutions, but is insoluble in ether; when heated it decomposes at about 180° C., yielding a small quantity of a red sublimate. Only the sodium hydrogen salt has been prepared in crystalline condition, and to this Dimroth ascribes the formula $C_{20}H_{12}O_{10}Na_2 . C_{20}H_{13}O_{10}Na$, whilst he concludes that the acid has the composition $C_{20}H_{14}O_{10}$, and not $C_{16}H_{12}O_8$, as previously supposed.

Although no distinction is to be observed in the absorption spectra of the aqueous and alkaline solutions of laccaic and carminic acids, it is possible when the colouring matters are dissolved in sulphuric acid to discriminate between them in this way. When fused with potassium hydroxide, laccaic acid gives, in addition to a substance (*a*) volatile in steam, colourless needles, melting-point 142—143° C.; a compound (*b*) $C_{10}H_6O_6$, or $C_{10}H_8O_6$, melting-point 285° C., readily soluble in water; a compound (*c*) $C_8H_8O_3$, melting-point 169° C., possibly a hydroxytoluic acid; and (*d*) an easily soluble substance, the aqueous solution of which gives a black coloration with ferric chloride (Schmidt).

Reduction of laccaic acid with tin and hydrochloric acid, or with zinc-dust and aqueous ammonia, yields a compound $C_{20}H_{16}O_9$, which crystallises in brown-yellow rhombohedra, and which on oxidation by means of cupric chloride and hydrochloric acid, yields a substance of the composition $C_{20}H_{14}O_9$, which Dimroth considers is related to the former substance as quinone to hydroquinone.

Although laccaic acid does not yield crystalline bromination products similar to *a* and *β*-bromocarmine, compounds of this nature have been obtained by Dimroth from its oxidation product, calaic acid.

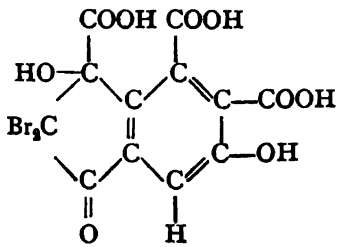
Calaic acid is produced when laccaic acid is oxidised by means of hydrogen peroxide (2½—3 molecular proportions) in the presence of a catalyst (cobalt, manganous, cerous, or ferrous salts; manganous chloride is best). This acid, $C_{18}H_{14}O_{11}$, crystallises from ether in small yellow prisms, and from water in needles having the composition $C_{18}H_{14}O_{11}$, $2\frac{1}{2}H_2O$. It does not possess dyeing properties, contains one carbonyl and three carboxyl groups, and may be purified by means of its crystalline barium salt. A silver salt, $C_{18}H_{12}O_{11}Ag_2$, has also been prepared.

When calaic acid is brominated, in glacial acetic acid, two products are formed: (i) an *α*-ketonic acid, $C_{12}H_{10}O_6Br_2$, and (ii) *β*-bromolaccain, $C_{12}H_5O_8Br$, these products being separated by taking advantage of the solubility of the latter in cold acetone.

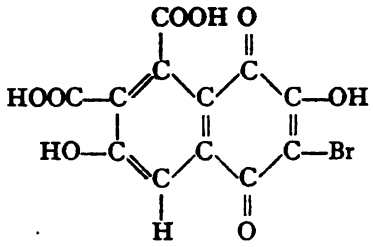
The α-ketonic acid forms brown-yellow crystals, melting-point 208—209° C., it gives an impure red-violet colour reaction with ferric chloride, and when heated to 80—90° C. with concentrated sulphuric acid, it loses carbon monoxide, yielding a monobasic acid, $C_{11}H_{10}O_5Br_2$, which has melting-point 245—246° C. (decomposition), and gives an intense violet colour reaction with ferric chloride. The keto acid forms a phenyl-hydrazone and semicarbazone, and, by treatment with methyl alcoholic hydrobromic acid, it yields the hydrobromic acid compound of its methyl ester, $C_{13}H_{12}O_6Br_2 . HBr$, colourless needles, melting-point 133—134° C. (decomposition).

β-Bromolaccain separates from water in crystals that have the composition $C_{12}H_5O_8Br, 2H_2O$; it has melting-point 234—235° C. (decomposition). It dyes wool orange from an acid bath, and gives a strong red colour reaction with ferric chloride. The potassium salt, $C_{12}HO_8BrK_4, H_2O$, crystallises in hexagonal plates. Concentrated sulphuric acid and acetic anhydride produce *diacetyl-β-bromolaccain anhydride*, $C_{16}H_7O_9Br$, indicating that two hydroxy groups are present in the molecule, and that it also contains two carboxyl groups in the ortho position.

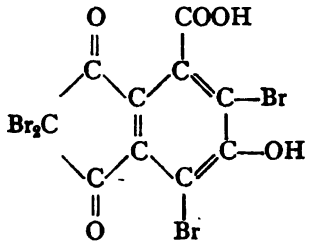
Oxidation of β-bromolaccain by means of hydrogen peroxide in warm glacial acetic acid yields two products, viz. (i) *hydroxy-tricarboxy-phenyl-glyoxylic acid*, and (ii) a compound $C_{12}H_6O_9Br_2$. The former, which is the chief product, crystallises in plates, melting-point 229·5—230° C. (decomposition), and on treatment with concentrated sulphuric acid at 130—140° C. yields a phenol-tetracarboxylic acid which melts at 212—214° C. (decomposition). The second oxidation product of β-bromolaccain has melting-point 188—190° C. (decomposition), and readily loses bromine; for it Dimroth tentatively proposes the formula—



For β-bromolaccain itself Dimroth and Goldschmidt suggest the structure—



and for this they find support in the fact that it resembles 2 : 6 : dihydroxy-α-naphthoquinone in its colour reactions. Moreover, it behaves very similarly to β-bromocarmine in that it yields an indone derivative, *α-bromolaccain* (cf. α-bromocarmine), when its boiling solution in water is treated with bromine :—



This compound crystallises in colourless needles, and yields 2 : 6-dibromphenol-3 : 4 : 5-tricarboxylic acid, melting-point 257—258°, and bromoform when treated with sodium hypobromite.

Dyeing Properties.—The dyeing properties of lac dye are practically identical with those of cochineal, but the shades obtained are somewhat faster. Owing to the resinous and mineral impurities accompanying the colouring matter, it is not readily soluble in water, and before use it is therefore ground to a paste with the requisite quantity of tin spirit together with a little hydrochloric acid, and allowed to stand overnight. Cochineal and lac dye can be used together with advantage, or after the wool is dyed with lac it may be entered into a fresh bath with cochineal. Its employment at the present time is, however, extremely limited.

Fowler (Indian Textile Jour., 1917, 244) has made attempts to standardise various Indian colouring matters so that they may be marketed in uniform strengths. It would appear that "Lac dye" is one of those with which he has been concerned.

KERMES.

Kermes is the most ancient dyestuff on record, for it was known in the time of Moses, and is mentioned in Scripture by its Hebrew name, "tola" or "tolaschani". According to Tychsen (Bancroft's "Philosophy of Permanent Colours," 1, 394), "the scarlet or kermes dye was known in the East in the earliest ages before Moses, and was a discovery of Phœnicians in Palestine, but certainly not of the small wandering Hebrew tribes". Under the name "coccus" it is frequently referred to by the Greek and Latin writers.

Kermes is an insect found on the oak kermes (*Quercus coccifera*, Linn.), and when living the female insects, which are fixed to the twigs of the tree, resemble bluish berries, and are covered with a whitish powder. As soon as their eggs are on the point of hatching these insects should be collected, killed by exposure to the steam of vinegar, and dried, and the product has then the appearance of pale reddish-brown grains. According to Bancroft, it would require 10 or 12 lbs. of kermes to produce the effect of a single lb. of cochineal.

Kermesic acid, $C_{18}H_{12}O_8$, the colouring matter of kermes, was first isolated, in the crystalline condition, by Heisse (Arbeit. a. d. K. Gesundheitsamte, 1895, 513), and has since been examined by Dimroth (Ber., 1910, 43, 1387; and Annalen, 1913, 399, 43). To isolate the kermesic acid, the kermes is first extracted with ether to remove wax, and this has been examined by Dimroth and Sherndal (Annalen, 1913, 399, 43), and identified as ceryl cerotate, $C_{52}H_{104}O_2$. The residue is then allowed to stand overnight with an ethereal solution of hydrochloric acid, by which means the kermesic acid, which exists in kermes in the form of a salt, is liberated and made capable of removal by repeated extraction with ether. For the purification of the substance, it is converted into its sparingly soluble sodium salt, which allows of its separation from *flavo-kermesic acid*,—a substance stated by Dimroth to be present in kermes dye to the extent of about 0·06 per cent. —the sodium salt of this being soluble in hot 2N sodium acetate solution, whereas the disodium salt of kermesic acid is almost insoluble. The sodium salt when dissolved in boiling sodium hydroxide solution and treated, whilst boiling, with excess of hydrochloric acid, yields a crystalline precipitate of kermesic acid.

Thus obtained, the acid consists of brick-red needles which decompose, without melting, at about 250° C. It is distinguished from carminic acid by the fact that it is soluble in ether, and is much more

sparingly soluble in cold water. On the other hand, the colour of the alkaline solutions of both colouring matters is practically identical. Kermesic acid is soluble, without decomposition, in concentrated sulphuric acid giving a violet-red solution, which, on addition of boric acid, becomes clear blue,—if flavo-kermesic acid is present as impurity only a dull bluish-violet results.

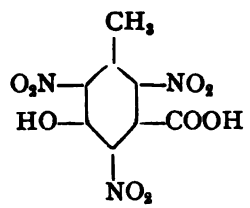
Disodium kermesate, $C_{18}H_{10}O_9Na_2$, prepared by means of sodium acetate, consists of a red-brown crystalline powder, sparingly soluble in water with a violet-red colour.

Barium kermesate, $(C_{18}H_{11}O_9)_2Ba$, is brown and contains water of crystallisation.

Tetra-acetyl kermesic acid, $C_{18}H_8O_9(C_2H_3O)_4$, yellow needles, melts at 245° C. *Kermesic acid trimethyl ether*, $C_{21}H_{18}O_9$, orange-red needles, melting-point 310° C., dissolves in sulphuric acid with a violet colour, and is prepared from the potassium salt by means of methyl sulphate in the presence of boiling toluene.

Flavo-kermesic acid, $C_{13}H_8O_6$, crystallises in needles, or prisms, and differs considerably from kermesic acid in its dyeing properties and in the colour of its solutions.

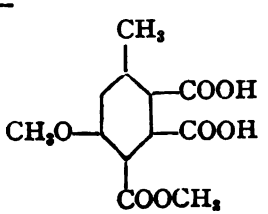
Kermesic acid is decomposed by warm concentrated nitric acid yielding *nitro-coccusic acid* (trinitro-cresotinic acid), identical with the acid—



obtained in a similar way from carminic acid.

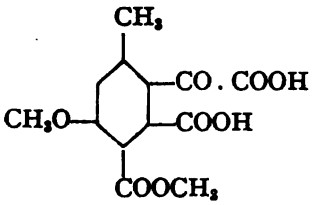
Kermesic acid contains no methoxy groups, and treatment with hydriodic acid gives the reduction product $C_{18}H_{12}O_8$, which decomposes at 275° C.

When oxidised with hot potassium permanganate, kermesic acid trimethyl ether produces two products, the one being *methylcochenillate monomethyl ether*—



which melts at 178—180° C., with formation of the anhydride, melting-point 149° C. Digestion with boiling potassium hydroxide (25 per cent.) solution converts this ester into *cochenillic acid methyl ether*, $C_{11}H_{10}O_7$, melting-point 200° C. (decomposition), whilst complete demethylation of ester, or acid, by means of hydriodic acid, yields hydroxyuvitic acid.

The second product of the oxidation is the *dimethyl ether* of *cresotinglyoxyl-dicarboxylic acid*—



melting-point 108—110° C. if anhydrous. The hydrated acid has melting-point 86° C., and this, by oxidation with alkaline permanganate, is converted into the above-described *methyl cochenillate methyl ether*.

When kermesic acid is heated with water at 150° C., carbon dioxide is evolved, and *decarboxykermesic acid*, $C_{17}H_{12}O_7$, is produced. This forms red needles (no melting-point), almost insoluble in sodium bicarbonate, soluble in caustic soda, and in concentrated sulphuric acid containing boric acid, yielding solutions which resemble, in colour, similar solutions of kermesic acid.

Bromination of kermesic acid yields (i) in boiling 50 per cent. acetic acid, *α-bromocarmin*; (ii) in boiling glacial acetic acid, *bromococcin*, $C_{16}H_9O_8Br$; (iii) in methyl alcohol, followed by treatment with concentrated hydrobromic acid, *tribromococcin*, $C_{15}H_7O_6Br_3$. (This product is also obtained when bromococcin is treated in the same way.)

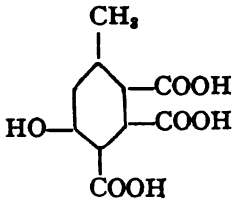
Bromococcin, $C_{16}H_9O_8Br$, crystallises in red needles, melting-point 259—260° C. (decomposition); it yields an acid potassium salt,

$$C_{16}H_9O_8Br . C_{16}H_8O_8BrK,$$

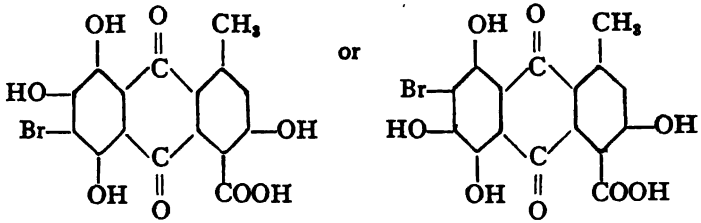
and a tetra-acetyl derivative,

$$C_{16}H_5O_8Br(CH_3CO)_4,$$

which forms yellow crystals. When oxidised by means of warm alkaline hydrogen peroxide, in the presence of a catalyst, bromococcin yields cochenillic acid:—

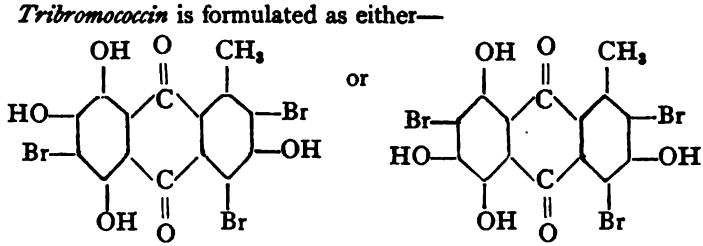


and from these facts Dimroth and Scheurer conclude that bromococcin has the structure—



either of which is in agreement with the fact that, in respect of its dyeing properties, it resembles purpurin, not anthragallol.

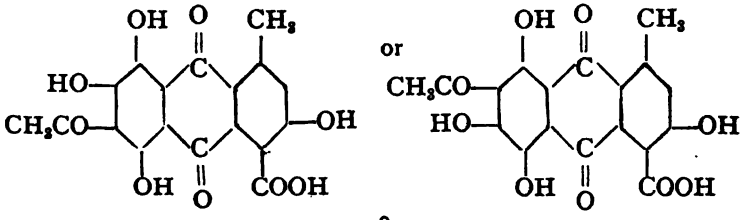
Tribromococcin is formulated as either—



It crystallises from acetic acid in long red needles, melting-point 245—248° C., is soluble in concentrated sulphuric acid giving a red-violet solution, the colour of which changes to deep blue when boric acid is added.

Tetra-acetyl-tribromococcin, $C_{15}H_3O_6Br(CH_3CO)_4$, crystallises in green-yellow needles, melting-point 223° C.; it yields nitro-coccusic acid when treated with fuming nitric acid.

Dimroth and Scheurer point out the close relationship that exists between bromococcin and kermesic acid, and assign to the latter the structure—



They support this by the results of the distillation of with zinc-dust, whereby they obtained α-methyl-ar from it prepared α-methyl-anthraquinone). They it probable that anthracene is simultaneously produ

Kermesic acid is thus closely related to carminic also considered by Dimroth to be a derivative of anth

Dyeing Properties.—According to Hellot (Bancrof of Permanent Colours," 1, 404), "the red draperies exhibited in the ancient Brussels and other Flemish all dyed with kermes". "The fine red or crimson c tapestries, which was originally called simply scarlet, t of *Venetian scarlet*, after the cochineal scarlet upon a discovered. . . ."

For the production of this scarlet, the wool, previ was mordanted with alum and tartar; and, accordin there is no evidence even in more recent years of th of a tin mordant in respect of this colouring matter, experiments he carried out indicated that by this la scarlet could be produced "in every respect as beautiful as any which can be dyed with cochineal".

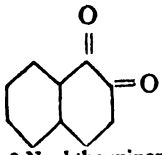
CHAPTER II.

THE NAPHTHOQUINONE GROUP.

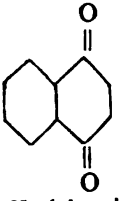
Introduction—Lapachol—Lomatiol.

INTRODUCTION.

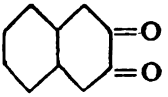
THERE are three possible naphthoquinones :—

(1) 

β-Naphthoquinone.

(2) 

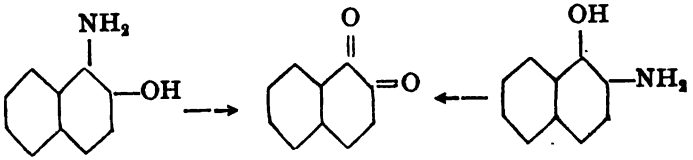
α-Naphthoquinone.

(3) 

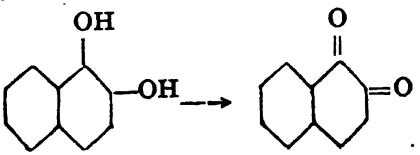
of which, however, only (1) and (2) are known.

Both of these quinones are readily formed by the oxidation of various naphthalene derivatives, the latter also from naphthalene itself.

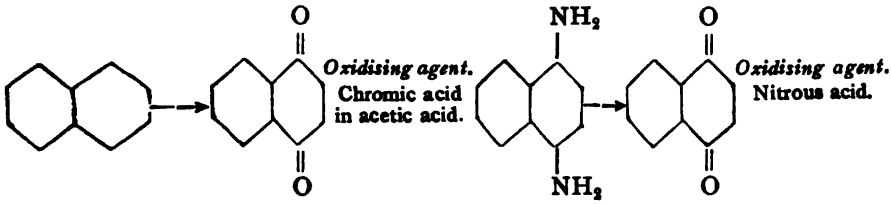
As starting-point for the production of β-naphthoquinone, either 1-amino-2-naphthol or 2-amino-1-naphthol may be used, and the former when oxidised by means of chromic acid, or, better, ferric chloride, gives an almost theoretical yield of the quinone :—

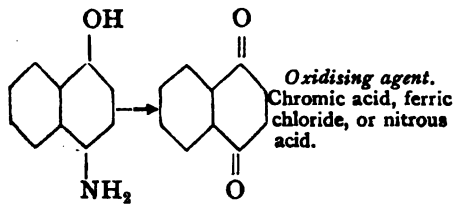


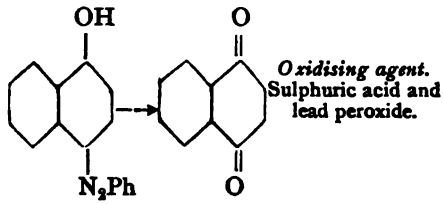
Not only the amino-naphthols, but also 1-2-dihydroxy-naphthalene may be oxidised by means of ferric chloride with production of the β-quinone :—



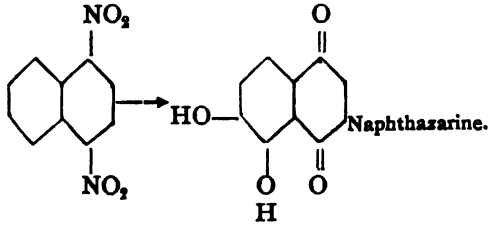
For the production of the second known naphthoquinone, naphthalene, or a variety of its α-mono, or 1 : 4-di- substitution products may form the starting-point, and various examples are represented by the following formulæ, the oxidising agent employed being stated in each case :—



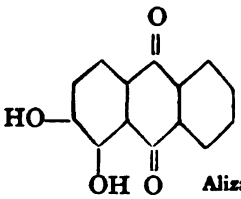




The synthetic colouring matter naphthazarine, a dihydroxy derivative of this quinone, is of commercial value, and may be prepared by the action of zinc and sulphuric acid, or suphur and oleum, on 1 : 4 : dinitro-naphthalene, the change being represented thus :—



The relationship that exists between this compound and alizarin is worthy of note—



Alizarin.

The naturally occurring colouring matters of the naphthoquinone group are but few in number, and are not widely distributed.

LAPACHOL.

This colouring matter has been obtained from the wood of the Lapacho tree, from Greenheart wood, and also from Bethaberra wood. It was from the first-named that Arnaudon (Comptes rend., 1858, 46, 1154) originally obtained it by extracting the wood with alcohol, and recrystallising the product from a mixture of alcohol and ether. Stein (J. f. pr. Chem., 99, 1) showed that the same colouring matter was present in Greenheart wood, whilst Green and Hooker (Amer. Chem. Jour., 11, 267) obtained it from Bethaberra wood.

According to Paternò (Gazetta, 12, 337; 21, 374) the colouring matter is best extracted from the wood by means of soda solution (1 gram soda crystals in 16 grams water for 20 grams finely divided wood), the product being precipitated from the combined extracts by means of hydrochloric acid, purified by extraction with barium hydroxide solution and reprecipitation with acid. The product thus obtained when recrystallised from benzene is readily obtained in a pure condition.

Lapachol, $C_{15}H_{14}O_3$.—The melting-point of the crystalline product has been variously stated as 138° C. (Paternò) and 140·5° C. (Green). It is insoluble in water, but soluble in alkalis, yielding red solutions which contain its salts. It is not very soluble in ether, but easily soluble in chloroform, glacial acetic acid, and in hot alcohol or benzene.

Monoacetyl derivative, $C_{15}H_{13}O_3Ac$, yellow prisms, melting-point 82—83° C., is prepared by the action of acetic anhydride and sodium acetate on lapachol. It is insoluble in water, crystallises from alcohol and is very easily hydrolysed; cold nitration converts it into *nitro-acetyl-lapachol*, $C_{15}H_{12}O_3(NO_2)Ac$, melting-point 166—168° C., whilst further acetylation yields a *diacetyl-derivative*, $C_{15}H_{12}O_3Ac_2$, colourless crystals, melting-point 131—132° C.

Various salts of lapachol have been described, of which those of the metals are red in colour, those of organic bases yellow to orange. The sodium and potassium salts crystallise with $5H_2O$:

$$C_{15}H_{13}O_3Na(K),\ 5H_2O;$$

the calcium, or strontium salt has only $1\frac{1}{2}H_2O$:

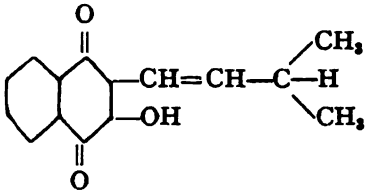
$$(C_{15}H_{13}O_3)_2Ca(Sr),\ 1\frac{1}{2}H_2O;$$

whilst the barium salt has $7H_2O$: $(C_{15}H_{13}O_3)_2Ba,\ 7H_2O$. Anhydrous lead, silver, and ammonium salts have also been described. Of the salts of organic bases, the aniline salt, $C_{15}H_{14}O_3 . C_6H_7N$, consists of yellow needles, melting-point 121—122° C., that of *p*-toluidine, $C_{15}H_{14}O_3 . C_7H_9N$, of orange-yellow leaflets, melting-point 130° C., and that of *o*-toluidine, $C_{15}H_{14}O_3 . C_7H_9N$, of yellow crystals, melting-point 135° C.

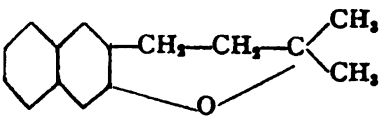
The elucidation of the constitution of this colouring matter is due to Paternò (Gazetta, 12, 337 and 622 (1883); 19, 601 (1890); and 21, 374 (1891)), and Hooker (Jour. Chem. Soc., 1892, 61, 611; 1896, 69, 1355).

It was Paternò who first put forward a structural formula for lapachol, which he based chiefly upon evidence obtained from examination of its oxidation and reduction products.

When oxidised by nitric acid (sp. gr. 1·38), lapachol gives rise to phthalic acid in good yield, whereas when the colouring matter is reduced by means of hydriodic acid and red phosphorus, a substance is obtained which Paternò considered to be β-isoamyl-naphthalene. As the result he suggested the following constitution for lapachol:—

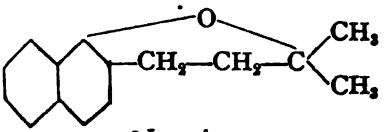


The position of the double bond has been disputed by Hooker. This author concludes that the product which Paternò considered to be β-isoamyl-naphthalene in reality consists of a mixture of two substances to which he gives the names *α* and *β-lapachan*, and formulates thus:—



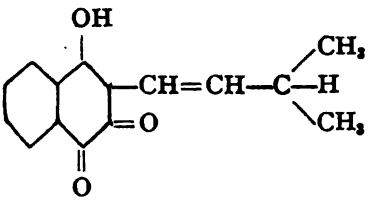
α-Lapachan.

and



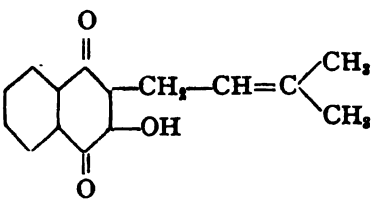
β-Lapachan.

He was able to show that the product obtained by treating naphthalene with isoamyl-chloride, in the presence of aluminium chloride, was not identical with that obtained by Paternò by the reduction of lapachol. Moreover, by condensation of *β-hydroxy-α-naphthoquinone* and *isovaleric aldehyde*, in the presence of hydrochloric acid, he obtained a compound that should have the structure applied to lapachol by Paternò, though to this, in view of its bright red colour, he assigned the formula—

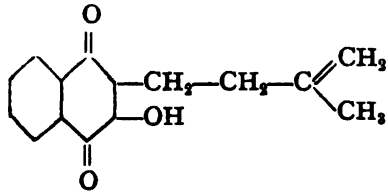


and the name *iso-β-lapachol.*

Although iso-β-lapachol is a derivative of β-naphthoquinone, whilst Paternò's formula for lapachol represents it as a derivative of α-naphthoquinone, both substances should yield the same reduction product, but as the reduction product given by iso-β-lapachol is not identical with that obtained by Paternò from lapachol, Hooker concluded that lapachol has in reality the structure—

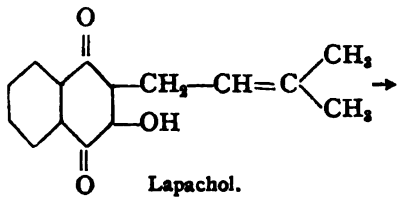


The alternative form—

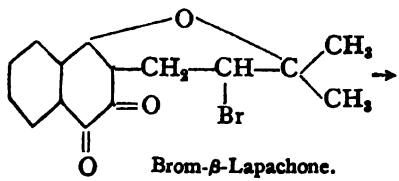


was rejected by Hooker, and a consideration of the following series of changes makes clear his ground for this rejection.

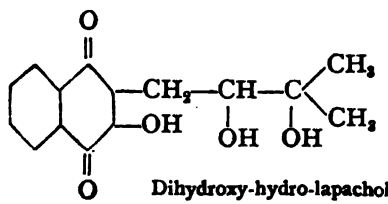
When lapachol is brominated, in chloroform, the product is *brom-β-lapachone*, orange-red crystals, melting-point 139—140° C. This when boiled with caustic soda yields *dihydroxy-hydro-lapachol*, melting-point 181—182° C., and, according to Hooker, on treatment of this product with concentrated sulphuric acid the products (1), (2), (3), and (4) are formed simultaneously, and the changes may be represented by the following scheme :—



Lapachol.

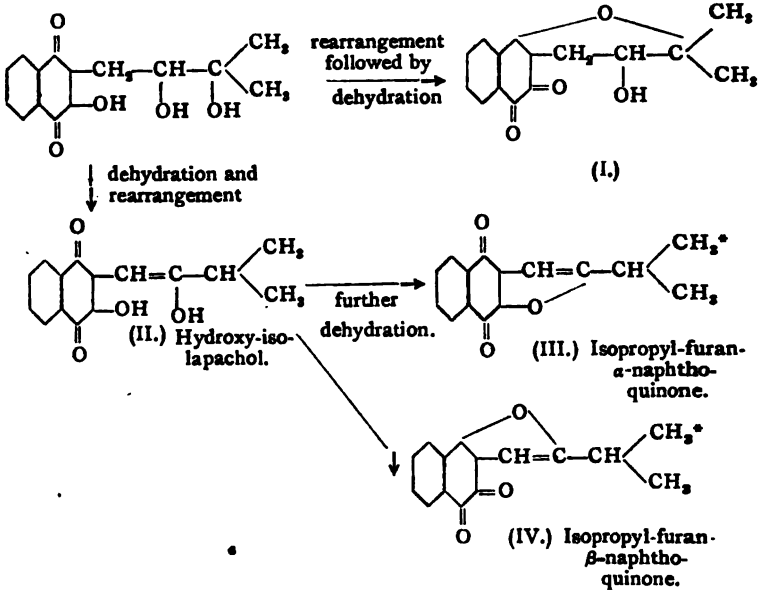


Brom-β-Lapachone.

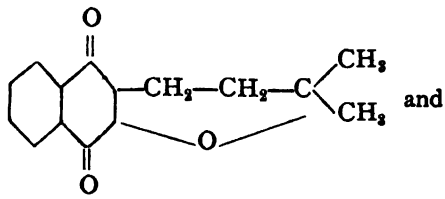


Dihydroxy-hydro-lapachol.

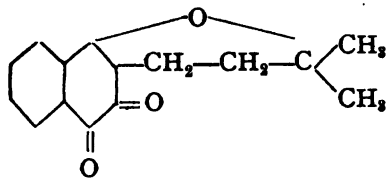
Then



When lapachol is treated with mineral acids, Hooker obtained two substances which he termed α and β-lapachone, and to which the following constitutions have been assigned :—



α-Lapachone.



β-Lapachone.

* Both of these substances can be reconverted by the action of caustic soda into dihydroxy-isolapachol though Hooker did not succeed in isolating this as an intermediate product in the initial reaction with sulphuric acid.

The former consists of pale yellow crystals, melting-point 117° C., and changes on solution in concentrated sulphuric acid into the latter, which forms orange-red crystals, melting-point 155—156° C.

According to Crosa and Manuelli (Rend. Accad. Linc., 1895, ii., 250), Lapacho wood, on prolonged distillation with steam, yields a volatile crystalline product to which they gave the name *Lapachonone*, and composition $C_{16}H_{16}O_2$, colourless crystals, melting-point 61·5° C. It is optically active; its picrate, $C_{16}H_{16}O_2 . C_6H_2(NO_2)_3OH$, melting-point 145° C.; on recrystallisation from alcohol forms products in which the proportion of picric acid is variable.

From lapachonone, by oxidation with dilute nitric acid, they obtained phthalic acid, whilst by the action of phosphorus pentachloride it was converted into *dichlor-lapachonone*, $C_{16}H_{14}Cl_2O_2$, large colourless prisms, melting-point 108° C., volatile with steam.

Bromination of lapachonone, in cold acetic acid solution, yields *brom-lapachonone*, $C_{16}H_{15}O_2Br$, colourless prisms, melting-point 126° C., together with small quantities of a *brom-dihydroxy-compound*, $C_{15}H_{15}O_4Br$, yellow prisms, melting-point 140° C., which forms almost the whole product when lapachonone is brominated in aqueous suspension. It yields a *diacetyl-derivative*, yellow plates, melting-point 132° C., and a phenyl-hydrazone, red crystalline crusts, which has no definite melting-point (Manuelli, Atti. Real. Accad. Lincei., 1900 (v.), 9, ii., 314).

LOMATIOL.

This colouring matter, which is closely related to lapachol, has been obtained from the seeds of the *Lomatia ilicifolia* and *Lomatia longifolia*, which occur in Australia (N.S.W. and Victoria).

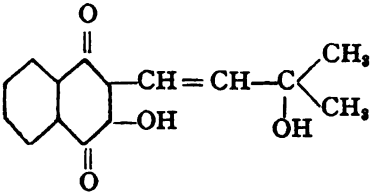
The colouring matter is obtained by extracting the seeds with boiling water acidified with acetic acid, and allowing the filtered extract to cool, when the product crystallises out. It is recrystallised from the same solvent.

Lomatiol, $C_{15}H_{14}O_4$, yellow needles, melting-point 127° C., is easily soluble in alcohol or ether, in alkalis and alkali carbonates.

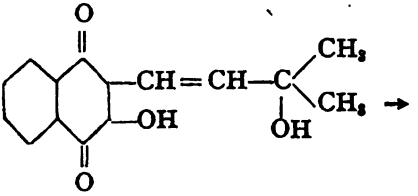
When heated with acetic anhydride and a trace of zinc chloride, it yields a *di-acetyl-derivative*, $C_{15}H_{12}O_4(C_2H_3O)_2$, yellow needles, melting-point 82°.

The salts of lomatiol vary in colour from orange to brown; thus the silver salt, $C_{15}H_{13}O_4Ag$, H_2O, is brown, the calcium salt, $(C_{15}H_{13}O_4)_2Ca$, is dark red, whilst the barium salt, $(C_{15}H_{13}O_4)_2Ba$, H_2O, is orange.

Rennie, who first examined this compound (Chem. Soc. Trans., 1895, 67, 784), was of the opinion that lomatiol was hydroxy-lapachol, but Hooker (Chem. Soc. Trans., 1896, 69, 1381), who continued Rennie's investigations, was able to show that it was *hydroxy-iso-lapachol*, and assigned to it the formula—

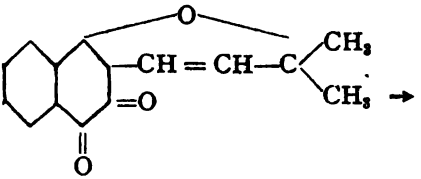


When lomatiol is dissolved in concentrated sulphuric acid, and left for some time, it passes into *hydroxy-β-lapachol* (3), red needles, melting-point 204° C., identical with that obtained from dihydroxy-hydro-lapachol by the action of the same reagent, whereas, if the reaction is stopped at an earlier stage, by pouring the solution of lomatiol in concentrated sulphuric acid into water almost as soon as solution is completed, an intermediate product, *dehydrolapachone*, is obtained to which Hooker gives the structure (2). The formation of these is shown thus:—

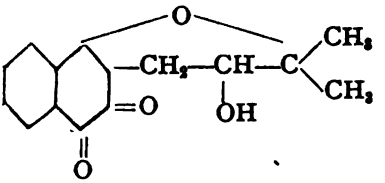


Lomatiol.

(2)



(3)



By careful oxidation of lomatiol, Rennie obtained acetic acid and phthalic acid.

DROSERA WHITTAKERI.

Drosera whittakeri is found in Australia, and grows plentifully on the hills near Adelaide. The tuber of this plant consists of an inner solid but soft nucleus full of reddish sap or juice, and an outer series of easily detached thin, and more or less dry, layers of an almost black material. Between these layers are to be found small quantities of a brilliant red colouring matter, the amount varying in tubers of different size and age, but apparently more plentiful in the older plants (Rennie, Chem. Soc. Trans., 1887, 51, 371; 1893, 63, 1083).

The colouring matter is extracted from the tubers by means of hot alcohol, the solution evaporated, and the residue, containing a little alcohol, is then mixed with water and allowed to stand. The product is dried, sublimed, and the brilliant vermilion powder, which contains two substances, is fractionally crystallised from boiling alcohol, or acetic acid.

The more sparingly soluble compound $C_{11}H_8O_5$ forms red plates, melts at 192—193°, dissolves in alkaline solutions with a deep red violet colour, and gives a *triacetyl derivative*, $C_{11}H_5O_5(C_2H_3O)_3$, melting-point 153—154°.

The *monosodium* compound $C_{11}H_7O_5Na$, $2H_2O$, gives dark reddish-brown needles, the *disodium* compound $C_{11}H_6O_5Na$, $2H_2O$, brown needles, and the *calcium* compound $(C_{11}H_7O_5)_2Ca$, $3H_2O$, dark brown crystals.

By treatment with stannous chloride or hydrochloric acid, this substance $C_{11}H_8O_5$ yields a reduction product $C_{11}H_{10}O_5$, in yellow needles, melting-point 215—217°. When dry, this is stable in air, but if left in contact with alcohol or water, it soon becomes red owing to oxidation. According to Rennie it is probable that the original colouring matter is a *trihydroxymethylnaphthoquinone*, in which case the substance $C_{11}H_{10}O_5$ will consist of the corresponding hydroquinone derivative. The more readily soluble compound contained in the tubers possesses the formula $C_{11}H_8O_4$. It crystallises in red needles, melting-point 174—175°; dissolves in alkaline solutions with a deep red coloration; and gives a *diacetyl* derivative, $C_{11}H_6O_4(C_2H_3O)_2$, in yellow needles, melting-point 107—110°.

CHAPTER III.

THE BENZOPHENONE GROUP.

Introduction—Benzophenone—Cotoïn—Phloretin—Maclurin.

INTRODUCTION.

THIS group contains but one product, maclurin, that is of tinctorial value, and this substance has but feeble dyeing properties. Maclurin, however, found considerable commercial use at one time in the form of its dis-azobenzene derivative known as "Patent Fustin".

Besides maclurin, a number of hydroxylated derivatives of benzophenone occur in nature, but they have no tinctorial value. It has, however, been thought advisable to introduce a brief account of the two most important of these, viz. cotoïn and phloretin, in particular, in view of the attempt made by Perkin and Martin (Chem. Soc. Trans., 1897, 1149) to obtain from them products of tinctorial value similar to "Patent Fustin".

BENZOPHENONE.

Benzophenone, the parent substance of this group, has been produced synthetically in a variety of ways, e.g. by distillation of calcium benzoate—

$$(C_6H_5COO)_2Ca = (C_6H_5)_2CO + CaCO_3,$$

by the action of phosphorus pentoxide on benzoic acid and benzene—

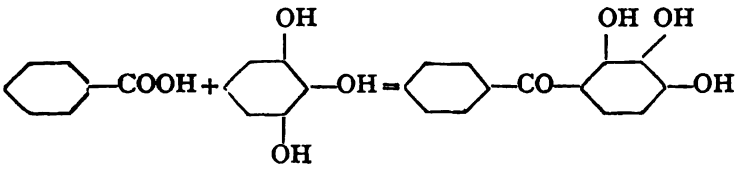
$$C_6H_6 + C_6H_5COOH - H_2O = C_6H_5CO \cdot C_6H_5,$$

or by the action of benzoyl chloride, or phosgene, on benzene, in the presence of aluminium chloride—

$$2C_6H_6 + Cl—CO—Cl = C_6H_5—CO—C_6H_5 + 2HCl, \text{ and}$$
$$C_6H_6 + C_6H_5—COCl = C_6H_5—CO—C_6H_5 + HCl$$

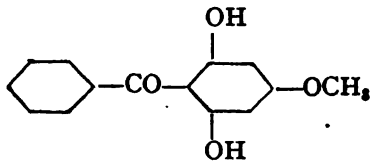
The pure substance occurs in two forms, viz. large rhombic prisms, melting-point 49° C. (stable), and monoclinic prisms, melting-point 26° C. (labile), (Auwers and Meyer, Ber., 1889, 22, 550); it boils at 306° C.

Of the poly-hydroxy derivatives of benzophenone, that obtained by heating together benzoic acid and pyrogallol in the presence of zinc chloride (D.R.P. 49149), or by the condensation of pyrogallol and benzotrichloride in the presence of alcohol (D.R.P. 54661), is a mordant colour of value, and is found in commerce as a paste under the name *Alizarin yellow A.* (B.A.S.F.). On alum it gives an orange-yellow shade, fast to light and washing. Its preparation may be represented thus:—



COTOÏN.

Benzoyl-phloroglucinol-mono-methyl ether, $C_{14}H_{12}O_4$, is found, to-



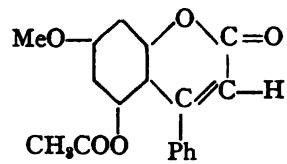
gether with various related substances, in true Coto bark, but not in para Coto bark, and has been the subject of much investigation by Ciamician and Silber (Ber., 24, 299 and 2977; 25, 1119; 26, 777; 27, 409 and 841; 28, 1549), Jobst (N. Repert. Pharm., 1876, xxv., 23; Ber., 11, 1031), Jobst and Hesse (Ber., 10, 249; Annalen, 199, 17), and Hesse (Ber., 26, 2790; 27, 1182; Annalen, 282, 191). As a result its constitution has been made clear and a number of its derivatives described.

Cotoïn can be isolated from true Coto bark by extracting the powdered bark with cold ether, distilling off the ether from the extract, and mixing the residue, whilst still hot, with light petroleum, whereupon a resinous-oily mass separates, from which the solution of cotoïn can be decanted and the product obtained from it in the form of large yellow crystals. A further quantity can be obtained from the resinous mass mentioned above by boiling it with lime-water, and treating the solution obtained with hydrochloric acid, when the cotoïn is precipitated. Cotoïn may be recrystallised from alcohol, or hot water, when it separates in yellow prisms, melting-point 130°—131° C. It is difficultly soluble in cold water, readily soluble in hot,

is fairly soluble in alcohol, ether, and chloroform, but sparingly soluble in light petroleum or benzene. It dissolves in alkalis forming yellow solutions from which it is reprecipitated on acidification. As decomposition products of cotoïn, phloroglucinol as also benzoic acid have been obtained.

Cotoïn has been used pharmaceutically in cases of diarrhœa and of phthisis.

The *diacetyl derivative*, $C_{18}H_{16}O_6$, produced by the action of acetic anhydride, or acetic anhydride and sodium acetate, on cotoïn, consists of large prisms, melting-point 94° C. If sodium acetate is used in the acetylation, the diacetyl derivative is accompanied by the acetyl derivative of *methoxy-hydroxy-phenyl-coumarin acetate*, melting-point 142° C.—



Benzoyl cotoïn, obtained by the action of benzoyl chloride on cotoïn, crystallises in prisms, melting-point 110°—112° C.

Dibenzoyl-cotoïn consists of needles, melting-point 134°—135° C.

Dimethyl-cotoïn, obtained by the action of methyl iodide and alkali on cotoïn, crystallises from alcohol, and has melting-point 138° C. It yields a mono-acetyl derivative, colourless needles, melting-point 150° C., hence the formula

$$HO \cdot C_6H \cdot Me(OMe)_2 \cdot CO \cdot C_6H_5$$

has been proposed for it by Ciamician and Silber.

Dibrom cotoïn, $C_{14}H_{10}O_4Br_2$, which crystallises in large colourless needles, melting-point 116° C., is prepared by the action of bromine on cotoïn in chloroform solution.

Cotoïn oxime, $C_{14}H_{13}NO_4$, crystallises in plates, soluble in alcohol, difficultly soluble in water, and has been prepared by the action of hydroxylamine hydrochloride on a cold aqueous solution of cotoïn in sodium carbonate.

Mono-nitroso-cotoïn consists of dark red leaflets, or orange-yellow needles (from acetic acid), melting-point 153—154° C. (both forms). The needle variety possibly contains acetic acid of crystallisations (Pollak, Monatsh., 1901, 22, 996).

A dilute solution of cotoïn in sodium carbonate is capable of coupling with diazonium compounds, and in this way Perkin and

Martin (Chem. Soc. Trans., 1897, 1149) have prepared the following derivatives :—

Cotoïn-azo-benzene, $C_{14}H_{11}O_4 . C_6H_5N_2$, crystallises from acetic acid in orange-yellow needles, melting-point 183—184° C.; it yields a *diacetyl* derivative, $C_{14}H_9O_4 . (C_2H_3O)_2 . C_6H_5N_2$, when treated with acetic anhydride and sodium acetate, scarlet needles, melting-point 155—156° C.; on treatment with hot alkalis the acetyl compound is hydrolysed with formation of the free azo compound.

Cotoïn-azo-o-toluene, similarly prepared from diazotised *o*-toluidine and cotoïn, orange-yellow needles, melting-point 203—204° C.

Cotoïn-azo-p-toluene consists of orange-yellow needles, melting-point 207—208° C.

Hydro-cotoïn, which occurs together with cotoïn, is a *dimethyl ether of trihydroxy-benzoyl-benzene*, $C_6H_5 . CO . C_6H_2(OH)(OMe)_2$.

A number of poly-hydroxy benzophenone derivatives, including products found in Coto bark and related to cotoïn, have been prepared by W. H. Perkin and Robinson (Proc. Chem. Soc.; 1906, 305).

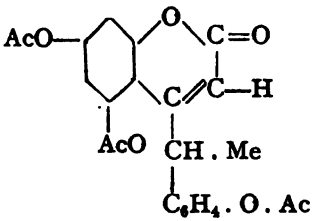
PHLORETIN.

Phloretin occurs in the form of two distinct glucosides, phloridzin and glycyphyllin, which are found in the root-bark of the apple, cherry, and plum-tree, and in the leaves of *Smilax glycyphylla* respectively (cf. Rennie, Jour. Chem. Soc., 1887, 634); whilst by catalytic hydrogenation of naringenin, in alcoholic solution with palladous chloride and hydrogen, Franck (Beitr. Phys., 1, 179; cf. Chem. Centrbt., 1914, ii., 253) obtained a dihydro-naringenin which he considered to be identical with phloretin.

Mrs. H. A. Michael (Ber., 1894, 27, 2686), in consideration of the fact that by fusion with alkali phloretin yields phloroglucinol and phloretic acid, whilst on acetylation with acetic anhydride and sodium acetate a product was obtained which appeared to be a triacetyl derivative, proposed the formula

$$C_6H_3(OH)_2 . O . CO . CH(Me) . C_6H_4OH$$

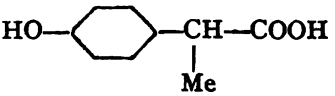
for phloretin. Ciamician and Silber (Ber., 1894, 27, 1627; 1895, 28, 1393), on further investigation of the product obtained by Michael, concluded that it was not a tri- but tetra-acetyl derivative, and found that when heated with excess of acetic anhydride and sodium acetate, it yielded *triacetyl-phloretyl-coumarin* by loss of one molecule of water—



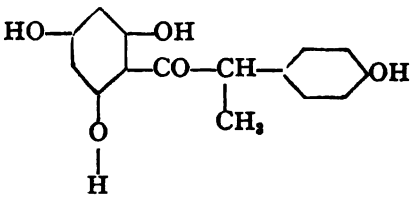
In this property the acetyl derivative of phloretin resembles the corresponding derivatives of maclurin and cotoïn. Ciamician and Silber, therefore, concluded that phloretin has the formula

$$C_6H_2(OH)_3 . CO . CH(Me) . C_6H_4OH$$

They also obtained a trimethyl-ether and tetra-methyl ether of phloretin in agreement with the above formula, and as phloretic acid has the structure



(Trinius, Annalen, 1885, *227*, *262*), that of phloretin may be represented thus :—



Phloretin, $C_{15}H_{14}O_5$, crystallises in shining prisms, melting-point 250° C. (decomp.), almost insoluble in cold water, only sparingly in hot, but crystallises out on cooling. It is easily soluble in alcohol and may be crystallised from a mixture of alcohol and water; it is soluble in ether or hot glacial acetic acid. In caustic alkalis, or carbonates, it dissolves with yellow coloration, but is reprecipitated on acidification. If dissolved in concentrated aqueous ammonia, and the solution allowed to stand, golden-yellow scales are deposited. When boiled with concentrated aqueous potassium hydroxide for about fifteen minutes it is decomposed with formation of phloroglucinol and phloretic acid.

The *tetra-acetyl derivative* melts at 95° C., and by loss of water when heated with acetic anhydride and sodium acetate, yields

Triacetyl-phloretyl-coumarin, $C_{23}H_{20}O_8$, which melts at 173° C.,

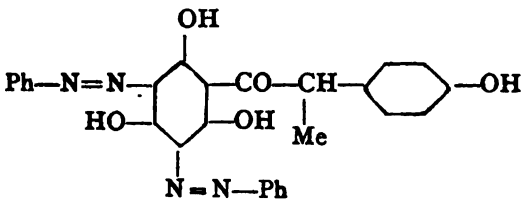
and from which *trihydroxy-phloretyl-coumarin*, $C_{17}H_{14}O_6$, melting at 213° C., may be obtained by hydrolysis.

Trimethyl-phloretin, $C_{18}H_{20}O_5$, yellow plates, melting-point 152° C., obtained by treatment of phloretin with methyl iodide and methyl alcoholic caustic potash, is accompanied, in the reaction product, by

Tetramethyl-phloretin, $C_{19}H_{22}O_5$, which can be obtained from the mother liquors after the separation of the trimethyl ether. It forms yellow plates, melting-point 58° C., and by treatment with hydriodic acid loses one methoxy group, passing to the trimethyl ether.

A. G. Perkin and Martin (Chem. Soc. Trans., 1897, 1152) have prepared the following dis-azo-derivatives of phloretin:—

Phloretin-disazo-benzene, $C_{15}H_{12}O_5(C_6H_5N_2)_2$, produced by adding excess of a solution of diazobenzene sulphate to a solution of phloretin in aqueous sodium carbonate, and consists of glistening red needles, melting-point 254—256° C. (decomp.). To this compound Perkin assigns the structure—



When acetylated by boiling with acetic anhydride and sodium acetate this substance yields *acetyl-phloretin-disazo-benzene*, orange-red needles, melting-point 217—219°. This product is sparingly soluble in acetic acid, and does not dissolve readily in cold dilute alkalis, but warm alkalis dissolve it, forming orange-red solutions which deposit the free azo compound on acidification.

Phloretin-disazo-o-toluene crystallises in red needles, melting-point 250—251° C.

MACLURIN.

This substance occurs, together with morin, in the wood of the tropical tree *Chlorophora tinctoria* (Gaudich), which comes into commerce as "Old Fustic".

The colouring matters of old fustic were first investigated by Chevreul ("Leçons de chimie appliquée à la teinture," ii., 150), who described two substances, one sparingly soluble in water, called

morin, and a second somewhat more readily soluble. Wagner (Jour. f. pr. Chemie, (1), 51, 82) termed the latter *moritannic acid*, and considered that it had the same percentage composition as morin. Hlasiwetz and Pfaundler (Annalen, 127, 351), on the other hand, found that the so-called moritannic acid was not an acid, and as moreover its composition and properties were quite distinct from those of morin, they gave it the name "Maclurin".

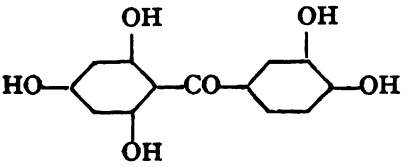
When morin is precipitated from a hot aqueous extract of old fustic by means of lead acetate the solution contains maclurin. After removal of lead in the usual manner, the liquid is partially evaporated and extracted with ethyl acetate, which dissolves the colouring matter. The crude product is crystallised from hot water or dilute acetic acid (Perkin and Cope, Chem. Soc. Trans., 1895, 67, 943). A crude maclurin is also obtained during the preparation of fustic extract, partly in the form of its calcium salt, and this product may be purified with dilute hydrochloric acid and crystallised from water. In order to decolorise the crystals, acetic acid is added to a hot aqueous solution and a little lead acetate in such quantity that no precipitate is formed, and the solution is then treated with sulphuretted hydrogen. The clear liquid thus obtained is much less strongly coloured, and after repeating the operation two or three times, the maclurin, which crystallises out on standing, possesses only a pale yellow tint.

Maclurin, to which the composition $C_{13}H_{10}O_6$ was assigned by Hlasiwetz and Pfaundler (Jahresber., 1864, 558), consists, when pure, of almost colourless needles, which contain one molecule of water of crystallisation; the anhydrous compound melts at 200° C. (Wagner, Jahresber., 1850, 529). The colouring matter is somewhat soluble in boiling water, is soluble in aqueous alkalis, forming pale yellow solutions, whilst with ferric chloride its aqueous solutions give a greenish-black coloration, and with aqueous lead acetate a yellow precipitate, which is soluble in acetic acid. When boiled with potassium hydroxide maclurin yields phloroglucinol and protocatechuic acid.

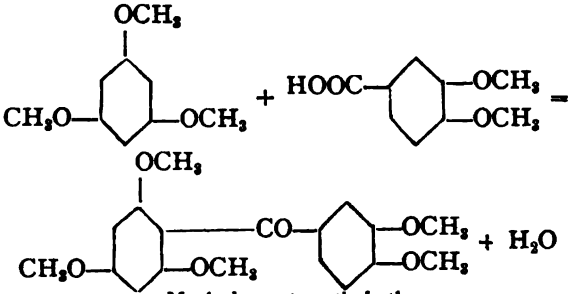
Pentabenzoyl-maclurin, $C_{13}H_5O_6(C_7H_5O)_5$, which melts at 155—156° C., was prepared by König and v. Kostanecki (Ber., 1894, 27, 1996), and *tribrom-maclurin*, $C_{13}H_7Br_3O_6 . H_2O$, colourless needles, by Benedikt.

Maclurin-pentamethyl-ether, $C_{13}H_5O(OCH_3)_5$, forms colourless leaflets which melt at 157° C.

König and v. Kostanecki first assigned to maclurin the constitution of a *penta-hydroxy-benzophenone* :—

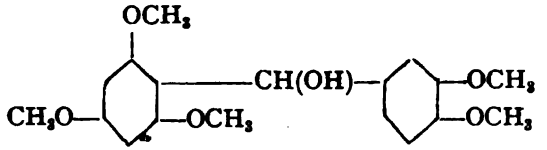


This is supported by the synthesis by W. H. Perkin and Robinson (Chem. Soc. Proc., 1906, 22, 305), and somewhat later by v. Kostanecki and Tambor (Ber., 1906, 39, 4022), of maclurin pentamethyl ether, by the interaction of veratric acid and phloroglucinol trimethyl ether in the presence of aluminium chloride. The reaction may be represented thus :—



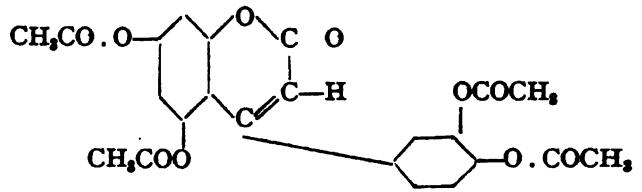
Maclurin-pentamethyl-ether.

When maclurin pentamethyl ether is digested with alcoholic potash and zinc-dust, *leucomaclurin-pentamethyl ether* (v. Kostanecki and Lampe, Ber., 1906, 39, 4014) is produced, prismatic needles,



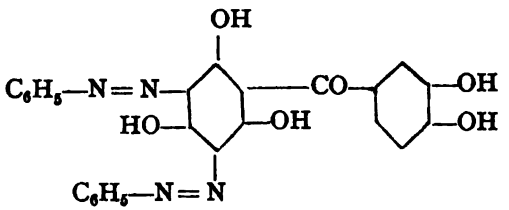
melting-point 109—110° C., and this on further reduction gives *penta-methoxy-diphenyl-methane*, melting-point 107—108° C. On the other hand, if leucomaclurin-pentamethyl ether is oxidised in acetic acid solution, *veratric acid* and *dimethoxy-benzoquinone* are formed.

By treatment of maclurin with acetic anhydride and sodium acetate, Ciamician and Silber (Ber., 27, 1628, and 28, 1393) obtained a crystalline product which has the composition of a penta-acetyl-maclurin less one molecule of water, viz. $C_{23}H_{16}O_{10}$, and to this compound the following constitutional formula has been ascribed, one of the acetyl groups having undergone condensation with the production of a coumarin derivative, *tetra-acetyl-tetra-hydroxy-phenyl-coumarin* :—



Patent Fustin.—Under the name "patent fustin" a colouring matter has been placed on the market, which consists chiefly of diazobenzene-maclurin (C. S. Bedford, 1887; Eng. Pat. 12667). To prepare this substance, old fustic is extracted with boiling water, the solution is decanted from the precipitate of morin and its calcium salt which separates on cooling, and is neutralised with the necessary quantity of sodium carbonate. Diazobenzene sulphate is then added until a precipitate no longer forms, and this is collected and washed with water. It is sold in the form of a paste, and dyes chrome mordanted wool an orange-brown shade.

Diazobenzene-maclurin (Bedford and Perkin, Chem. Soc. Trans., 1895, 67, 933; *ibid.*, 1897, 71, 186), which crystallises in salmon-red prismatic needles, melting-point 270° C. (decomp.), has the following constitution :—



It dyes wool and silk direct from a weakly acid bath, in shades of orange, and on mordants gives colours varying from orange-red on aluminium and orange-brown on chromium, to olive on iron. The dyeings are fairly fast to washing.

With acetic anhydride it yields a *tri-acetyl-derivative* only, $C_{18}H_5O_5(C_6H_5N_2)_2 . (C_2H_3O)_3$, orange-red needles, melting-point 240—243° C. (decomp.), which is in keeping with the fact that azobenzol-phloroglucinol yields only a mono-acetyl derivative when treated in like manner.

Dis-azo compounds of maclurin have also been prepared by coupling it with diazotised *o*- or *p*-toluidine, *p*-nitraniline, or sulphanilic acid, and the resulting compounds closely resemble the above described disazobenzene-maclurin.

Dyeing Properties of Maclurin.—With aluminium mordant maclurin gives a pale yellow, with chromium a yellow-green, and with iron a weak grey colour may be obtained.

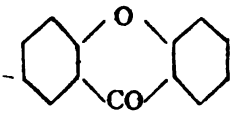
CHAPTER IV.

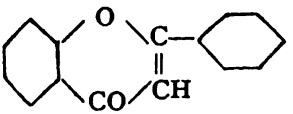
THE XANTHONE GROUP.

Introduction—Xanthone—Indian Yellow (Euxanthone)—Gentian Root (Gentisan).

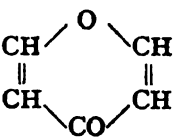
γ-PYRONE GROUPS.

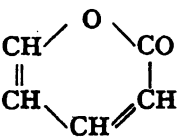
THE majority of the natural yellow colouring matters are derived either from xanthone (1) or flavone (2)—

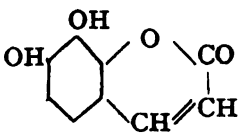
(1) 

(2) 

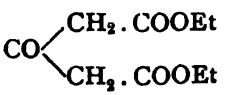
and the general properties of these compounds are due to their possession of the γ-pyrone nucleus (3). Colouring matters, on the other hand, containing the α-pyrone group (4), are as yet but little known, for hitherto only one, *daphnetin*, a dihydroxycoumarin, has been proved to exist (5)—

(3) 

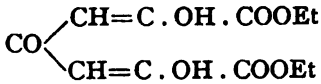
(4) 

(5) 

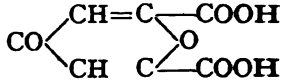
γ-Pyrone itself is the anhydride of a 1 : 5 dihydroxy 3 ketone and has been prepared synthetically by Claisen (Ber., 24, 118) from acetone dioxalic (chelidonic) ester—



This on treatment with fuming hydrochloric acid is converted into 2 : 6 γ-pyrone dicarboxylic acid (6)—

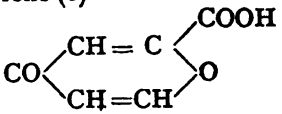


(6)



which passes on heating first into comenic acid (7) and subsequently into γ-pyrone (8)—

(7)



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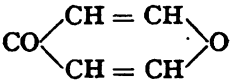
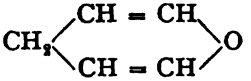


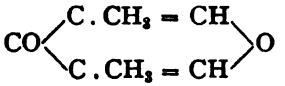
γ-Pyrone is colourless and melts at 32·5°.

The readiness with which many compounds containing the γ-pyrone or γ-pyran nucleus (8)—

(8)

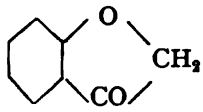


yield with mineral acids well-defined crystalline salts has long been known, having been observed in case of the phthaleins by Baeyer (Annalen, 1876, 183, 1), Fischer (Annalen, 1876, 183, 63), Nietzki and Schröter (Ber., 1895, 28, 50), by Perkin and Hummel, with hæmatein and brazilein (Ber., 1882, 15, 2337), and by Perkin with the flavones (Trans., 1896, 69, 439). These salts, which may be represented as addition products of the dyestuff with one molecule of mineral acid, are in general more highly coloured than the substances from which they are derived, and are, as a rule, very unstable in the presence of water. Various formulæ were at the time assigned to these compounds which appeared to possess a quinonoid structure. Collie and Tickle (Chem. Soc. Trans., 1899, 75, 710), however, observed that dimethyl γ-pyrone—



itself yields in this manner crystalline salts, as for instance $C_7H_8O_2HCl$; $C_7H_8O_2HNO_3(C_7H_8O_2)_2$; H_2PtCl_6, and suggested for the first time that their existence is to be ascribed to the quadrivalence of the oxygen atom. The experiments of Werner (Ber., 34, 1901, 33) supported this view, and it was subsequently shown by Baeyer and Villiger (Ber., 1901, 34, 2679) that all classes of organic compounds containing oxygen yield salt-like derivatives with complex acids, though the formation of compounds of this character with simple acids is of rarer occurrence.

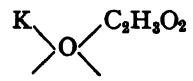
The phenolic colouring matters most distinctly reactive in this respect are those containing a γ-pyrone or γ-pyran nucleus, or an allied grouping, as, for instance, the keto-coumaran (coumaranone) derivatives of Friedländer and Rudt (*loc. cit.*)—



Not only mineral acids, but also simple organic acids may react in this manner, though the products derived from the latter are less easy to isolate.

With the haloid acids hydroxy anthraquinone derivatives do not appear to give oxonium salts, but the colour change which alizarin and other colouring matters of this group undergo by solution in strong sulphuric acid, is evidence of the formation of the corresponding sulphate. Except in the case of rufigallic acid (private communication—Perkin), which thus forms a beautiful crystalline sulphate, but from which, however, excess of sulphuric acid cannot be satisfactorily removed, no other oxonium salts of the anthraquinone series have as yet been isolated. Oxonium salts of the simple hydroxy ketones with mineral acids are also difficult to prepare.

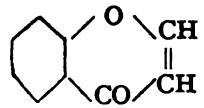
A second reaction, possibly due in its inception to the formation of oxonium compounds, is the behaviour of phenolic colouring matters in general in the presence of alcohol towards the alkali salts of numerous organic acids, more especially those of acetic acid (Perkin, Chem. Soc. Trans., 1899, 75, 433; 1903, 83, 130). In this manner the monopotassium salt of the colouring matter is, as a rule, obtained, but in certain cases the reaction does not proceed so far, there being produced an addition compound with the acetate or other alkali organic salt. These latter, which it is suggested are oxonium salts of the type—

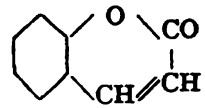


may represent the first stage of the reaction in all cases, the compound ultimately suffering conversion with liberation of acetic acid into the mono-alkali salt above referred to. These two reactions have proved of considerable service in the past, not only for the isolation of natural colouring matters, but as an indication of their molecular weight.

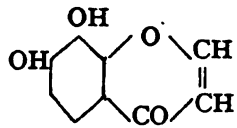
Chromone.

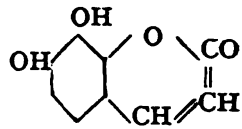
Colouring matters derived from chromone or pheno γ-pyrone (1), the analogue of coumarin (2)—

(1) 

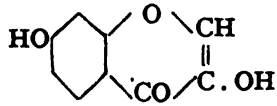
(2) 

or pheno *a*-pyrone, have not as yet been found in nature, though an hydroxy chromone (1) analogous to daphnetin (2) will no doubt possess dyeing properties and yield a yellow shade on aluminium mordant—

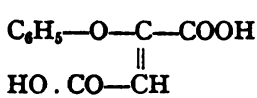
(1) 

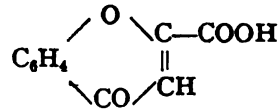
(2) 

Chromone is more specially interesting in connection with this subject owing to the isolation of the 3 hydroxy-chromonol—

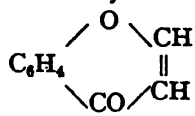


by Schall and Dralle (Ber., 1881, 21, 3009) as one of the products of the alkaline oxidation of brazilein. Benzo γ-pyrone derivatives were first synthesised by v. Kostanecki (Ber., 1900, 1998), but the synthesis of chromone itself is due to Ruhemann and Stapleton (Chem. Soc. Trans., 1900, 1179). When phenoxyfumaric acid (1) is treated with sulphuric acid benzo γ-pyrone carboxylic acid is produced (2)—

(1) 

(2) 

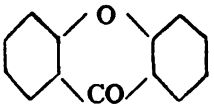
and this when heated in a vacuum yields benzo γ-pyrone—



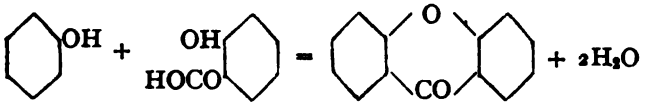
It crystallises in colourless needles, melting-point 59°, and its yellow solution in cold sulphuric acid possesses a blue fluorescence. An account of other synthetical methods applicable to chromone derivatives, which are of the same character as those employed for the preparation of flavone compounds, is given in the section devoted to these latter colouring matters.

XANTHONE.

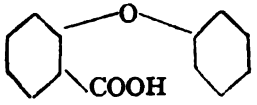
Xanthone or dipheno γ-pyrone—

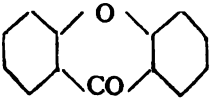


known also as diphenylene ketone oxide, benzophenone oxide, carbodiphenylene oxide, $C_{13}H_8O_2$, was first prepared by Kolbe and Lautermann (Annalen, 1860, 115, 197), by the action of phosphorus oxychloride on sodium salicylate and has been subsequently obtained from salicylic acid and its derivatives by the employment of various dehydrating agents. The most convenient method consists in distilling a mixture of acetic anhydride and salicylic acid (W. H. Perkin, Chem. Soc. Trans., 1883, 43, 35; cf. also Graebe, Annalen, 254, 265), when the higher boiling fraction on cooling deposits crystals of xanthone. During the reaction some phenol is produced and is indeed found to some extent in the distillate, and the reaction though probably more complex, may be considered to consist of the condensation of phenol and salicylic acid with formation of the xanthone.



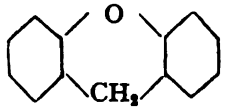
Phenyl salicylate (Siefert, J. f. prakt. Chem., (ii.), 31, 472) by long digestion at the boiling temperature yields xanthone, and it is also produced when salicylic acid phenyl ether, $COOH . C_6H_4 . O . C_6H_5$, is warmed with sulphuric acid (Graebe, Ber., 21, 503). Other methods of this type have been described by Richter (J. f. prakt. Chem., (ii.), 28, 275), Jeiteles (Monatsh., 17, 66), Staedel (Annalen, 283, 179), Goldschmiedt (Monatsh., 4, 123), and Klepl (J. f. prakt. Chem., (ii.), 28, 217). Fosse (Comptes rend., 1903, 136, 1006) has also obtained xanthones by warming the phosphoric esters of phenols with potassium carbonate. For the theory of xanthone formation the paper of Strohbach (Ber., 34, 4136) should be consulted. Ullmann and Zlokasoff (*ibid.*, 1905, 2111), by the interaction of sodium phenoxide and sodium *o*-chlorbenzoate in the presence of copper powder, obtained *o*-phenoxybenzoic acid (1) which by elimination of water passes into xanthone (2).

(1) 

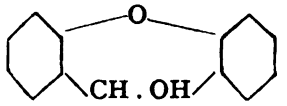
(2) 

Xanthones of the anthraquinone series can be prepared by the action of condensing agents on phenyl, naphthyl, or anthraquinonyl esters of 1 hydroxyanthraquinone 2 carboxylic acids (D.R.P. 251696).

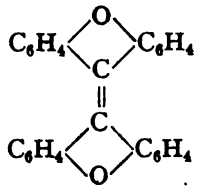
Xanthone crystallises in long colourless needles, melting-point 173—174° and dissolves in sulphuric acid to form a blue fluorescent liquid. The oxonium salts *xanthone hydrobromide*, $C_{13}H_9O_2Br$, and *xanthone stannichloride*, $(C_{13}H_8O_2)_2SnCl_4$, have been obtained by Gomberg and Cone (Annalen, 1910, 376, 183). By distillation with zinc-dust or by the action of fuming hydriodic acid at 160°, it is converted into *xanthene* (methylene diphenylene oxide) or dipheno γ-pyran—



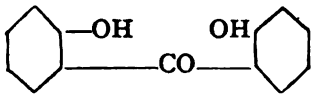
which may also be regarded as the anhydride of 2·2[1] dihydroxydiphenylmethane. By oxidation with chromic acid, xanthone can be reproduced (Merz and Weith, Ber., 14, 192). With boiling alcoholic soda and zinc-dust xanthone gives *xanthydrol* (Meyer and Saul, Ber., 26, 1276)—



and with zinc-dust and acetic acid *dioxy-xanthylene* (Gurgenganz and v. Kostanecki, Ber., 28, 2310) is produced—



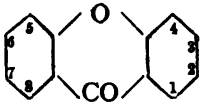
Fusion with alkali gives *xanthonic acid*, dihydroxybenzophenone



and from this by means of dehydrating agents xanthone can again be reproduced. The disruption of the γ-pyrone ring in this manner by the action of hydrolytic agents is characteristic of compounds containing this and the γ-pyran nucleus. In the flavone group this hydrolysis takes place even more readily, and to this to some extent

may no doubt be ascribed the lack of permanence of these colouring matters when applied to fabrics as compared with those of the anthraquinone group.

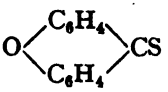
Interesting is the fact that when ketone colouring matters, and indeed all hydroxyketones, are alkylated in the usual manner with alkyl iodide and alcoholic potash, the hydroxyl in the ortho position to the carbonyl group remains unaffected, a fact which may be considered as an example of steric hindrance. This, at first pointed out by Herzig (Monatsh., 12, 161) in connection with the ethylation of euxanthone (dihydroxyxanthone) and quercetin, was observed by v. Kostanecki and Dreher (Ber., 26, 71) to be the property of all xanthones containing hydroxyls in the position 1 or 8,



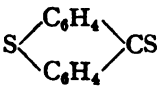
and the non-reactivity of the hydroxyl in this position has served in many cases as an indication of the presence of a carbonyl group. Such partially methylated compounds are as a rule insoluble in aqueous alkali, but give with alcoholic potash insoluble salts, which are readily hydrolysed with water. It has, however, been shown by Perkin in special instances that the alkylation of this hydroxyl group can be readily effected if a considerable excess of the reagents be employed, and it is probable that this method is of a general application (Chem. Soc. Trans., 1913, 103, 1632).

a-Dinitroxanthone, melting-point 190° (Richter, *loc. cit.*; Graebe, *loc. cit.*), *b-dinitroxanthone*, melting-point 262° (Perkin, Chem. Soc. Trans., 43, 189), *a-diaminoxanthone*, melting-point 209° (Graebe), *b-diaminoxanthone* (Perkin), *xanthone disulphonic acid* (Perkin), *monobromxanthone*, melting-point 125—127° (Graebe), *dibromxanthone*, melting-point 212° (Perkin), *xanthone phenylimine*, melting-point 134—135°, and *xanthone oxime* (Graebe and Röder, Ber., 32, 1689) have been directly prepared from xanthone.

3 *Nitro-xanthone*, melting-point 176°, 3 *chloroxanthone*, melting-point 171° (Ullmann and Wagner, Annalen, 1907, 355, 359), 3 *aminoxanthone*, melting-point 232°, 3 *methoxyxanthone*, melting-point 129°, 3 *hydroxyxanthone*, melting-point 243°, 1 *hydroxyxanthone*, melting-point 147° (Ullmann and Panchaud, *ibid.*, 350, 108), 2.4 *dinitroxanthone*, melting-point 206° (Ullmann, *ibid.*, 1909, 366, 79), 4 *chloroxanthone*, melting-point 130°, 4 *bromoxanthone*, melting-point 126° (Gomberg and Cone, *ibid.*, 1909, 370, 142), *xanthione*, melting-point 156° (Graebe and Röder)—



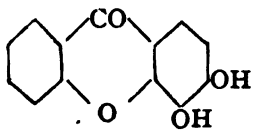
and *dithioxanthone*—

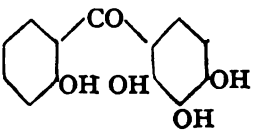


have been obtained indirectly.

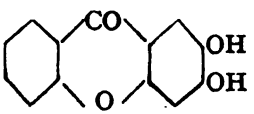
A general method for the preparation of the hydroxyxanthones consists of distilling a mixture of a phenol and an *o*-hydroxy-carboxylic acid with acetic anhydride, and this has been employed in numerous syntheses. In this manner 1 *hydroxyxanthone* (Michael, Amer. Chem. Soc., 5, 91; Graebe, Annalen, 54, 590), melting-point, 146—147°, 2 *hydroxyxanthone* (v. Kostanecki and Rutishauer, Ber., 25, 1648), melting-point 231°, 4 *hydroxyxanthone* (v. Kostanecki and Rutishauer), melting-point 224°, 3 *hydroxyxanthone* (v. Kostanecki and Nessler, Ber., 34, 3981), melting-point 243°, 3 : 6 *dihydroxy-xanthone* (isoeuxanthone) (v. Kostanecki, *ibid.*, 18, 1986), melting-point 243°, 2 : 5 *dihydroxyxanthone* (v. Kostanecki, *ibid.*, 27, 1991), melting-point 280°, and *gentisin* and *euxanthone*, the two natural representatives of this group, have been prepared.

These latter are both feeble dyestuffs, and this is explained by the fact that they do not possess two hydroxyls in the ortho position relatively to one another. Graebe and Eichengrun (Ber., 1891, 24, 969) obtained such a compound (1), 3 . 4 dihydroxy-xanthone by heating 2 . 3 . 4 . 2^1 tetrahydroxy-benzophenone (2) with water at 180—220°—

(1) 

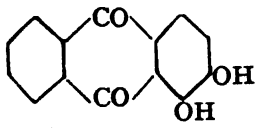
(2) 

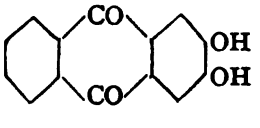
This melts at 240°, is a strong dyestuff giving on aluminium mordant yellow, and on iron mordant greyish-black shades. The position of the ortho-hydroxyl grouping is, however, of importance in that the 2 . 3 dihydroxy-xanthone of Liebermann and Lindenbaum (Ber., 1904, 37, 2728)—



and which is produced by the interaction of hydroxy-quinol and salicylic anhydride in the presence of sulphuric acid, is practically

devoid of dyeing property. As is well known, a similar distinction is to be observed between alizarine (1) and hystazarine (2)—

(1) 

(2) 

and it is of interest that similar rules (cf. Liebermann and v. Kostanecki) to those which are applicable to the hydroxy-anthraquinone dyestuffs, also hold good with the xanthone colouring matters. On the other hand, it will be observed later on, notably in the flavonol group of colouring matters, that ortho hydroxyls are not entirely essential for dyeing property. The statement by Tschirch and Polacco (Arch. Pharm., 1900, 238, 459) that a trihydroxyxanthone rhamnocitrin occurs in the berries of the *Rhamnus catharticus* has been shown by Oesch and Perkin (Chem. Soc. Trans., 1914, 105, 2350) to be incorrect.

Indian Yellow.

Indian yellow, Piuri, Purree, or Pioury, is a pigment mainly used in India for colouring walls, doors, and lattice-work, and by artists for water-colour work. On account of its disagreeable smell it is but rarely employed as a dyestuff. It is, or was, made almost exclusively at Monghyr in Bengal, and is obtained from the urine of cows which have been fed upon mango leaves. On heating the urine, usually in an earthen pot, the colouring matter separates out; this is pressed into a ball and dried partly over a charcoal fire and finally in the sun. It sold on the spot at about 1 rupee per lb. and is, or was, mainly sent to Calcutta and Patna. One cow produces, on the average, 3·4 litres of urine per diem, yielding 2 oz. (56 grams) of piuri. The yearly production is stated to have been from 100 to 150 cwts., which was probably over-estimated (*v.* Journ. Soc. Arts, 1883, (v.), 32, 16, and Annalen, 254, 268).

Piuri occurs in commerce in the form of round balls, which internally are of a brilliant yellow colour, whereas the outer layers are either brown or of a dirty green colour. The substance has a characteristic urinous smell. The undecomposed part consists only of *euxanthic acid* ($C_{19}H_{18}O_{11}$) in the form of a magnesium or calcium salt; the outer and decomposed portion contains in addition euxanthone, both free and combined. The composition of piuri seems to be variable; a fine sample, according to Graebe, contained

Euxanthic acid	51·0
Silicic acid and alumina	1·5
Magnesium	4·2
Calcium	3·4
Water and volatile matter	39·0
	99·1

Euxanthic acid is easily obtained by digesting piuri of good quality with dilute hydrochloric acid and treating the residue with a solution of ammonium carbonate. On the addition of hydrochloric acid to the filtered solution euxanthic acid crystallises out with $1H_2O$ in glistening straw-yellow needles, melting at 162°. Euxanthic acid is, according to Spiegel, decomposed by hydrochloric acid into glycuronic acid and euxanthone—

$$C_{19}H_{18}O_{11} = C_{13}H_8O_4 + C_6H_{10}O_7$$

Külz, in order to prove the animal origin of euxanthic acid, gave euxanthone to rabbits and dogs, and was able to detect euxanthic acid in the urine. Külz's experiments did not corroborate Schmid's statement that mangostin (obtained from *Garcinia mangostana*, Linn.) is similarly converted into euxanthic acid by animals (E. Külz, Zeitsch. Biol., 33, 475; J. Soc. Chem. Ind., 6, 507).

Although the potassium and sodium salts of euxanthic acid are of the type $C_{19}H_{17}O_{11}M$, the silver salt obtained from the potassium salt by silver nitrate has the composition $C_{19}H_{16}O_{10}Ag$, and is derived from an anhydride of the acid (anhydroeuxanthic acid); the methyl and ethyl esters prepared from the silver salt are of the same type (Graebe, Ber., 1900, 53, 3360).

Potassium euxanthate, $C_{19}H_{17}O_{11}K$, H_2O, crystallises readily from water, and is prepared by neutralising euxanthic acid with potassium carbonate.

Magnesium euxanthate, $C_{19}H_{16}O_{11}Mg$, $5H_2O$, is the main constituent of Indian yellow (Graebe, Annalen, 254, 268).

Barium euxanthate, $Ba(C_{19}H_{17}O_{11})_2$, $9H_2O$, is soluble in boiling water, and on cooling separates in the gelatinous condition.

Silver anhydroeuxanthate, $C_{19}H_{15}O_{10}Ag$, behaves similarly.

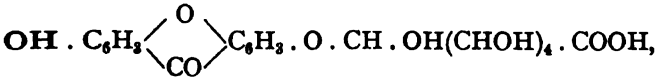
Ethylanhydroeuxanthate, $C_{19}H_{15}O_{10}C_2H_5$, yellow-coloured needles, melts at 198°.

Tetra-acetylethylanhydroeuxanthate, $C_{19}H_{11}O_{10}C_2H_5(C_2H_3O)_4$, colourless needles, melts at 216°.

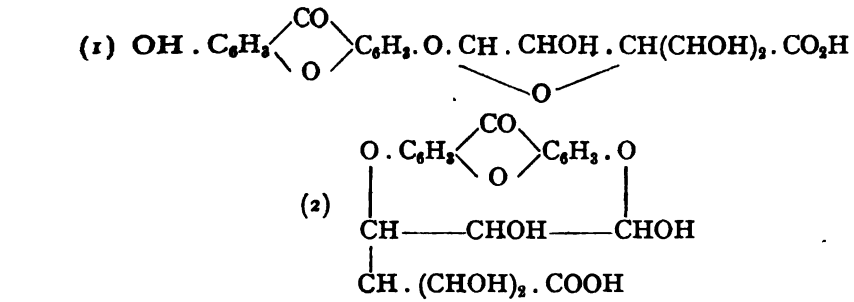
Methyl anhydroeuxanthate, $C_{19}H_{15}O_{10}CH_3$, melts at 218°, and closely resembles the ethyl derivative.

Benzoyl-anhydroeuxanthate, $C_{19}H_{11}O_{10}(CO—C_6H_5)_5$, melts at 194°, but has not yet been crystallised.

The constitution of euxanthic acid is expressed by Graebe (Annalen, 254, 267) as



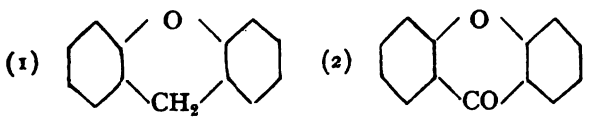
whereas for that of anhydroeuxanthic acid one of the following two formulæ is suggested:—



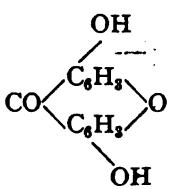
Euxanthone, *Purrenone*, *Purrone*, $C_{13}H_8O_4$, was first obtained by Stenhouse (Annalen, 51, 425), and soon afterwards by Erdmann (*ibid.*, 52, 365) from euxanthic acid. It crystallises in pale yellow needles or laminæ, melting at 240° (corr.), which sublime with little decomposition on gentle heating.

Diacetyl-euxanthone, pale yellow prisms (Salzmann and Wichelhaus, Ber., 1877, 10, 1397), melts at 185°.

By distillation with zinc-dust (Salzmann and Wichelhaus; Graebe and Ebrard, Ber., 16, 75) euxanthone gives *methylenediphenylene oxide* (1), which by oxidation is converted into xanthone (2), indi-

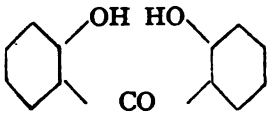


cating that euxanthone possesses the constitution of a *dihydroxy-*



xanthone (Salzmann and Wichelhaus).

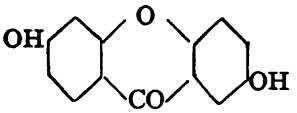
When fused with alkali euxanthone yields *euxanthonic acid*,



hydroquinone (v. Baeyer, Annalen, 155, 257), and resorcinol (Graebe, *ibid.*, 254, 265).

The first synthesis of euxanthone is due to Graebe (*loc. cit.*) who accomplished this by distilling a mixture of β-resorcylic acid and hydroquinone carboxylic acid, and it was shown later by v. Kostanecki and Nessler (Ber., 1891, 24, 3983), that if in this reaction the β-resorcylic acid is replaced by resorcinol the same product is obtained. As the result of these syntheses two constitutional formulæ for euxanthone were possible—

(1)



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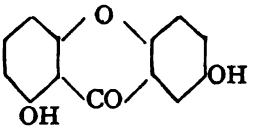
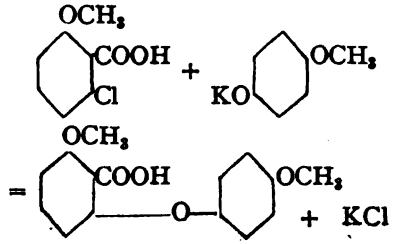
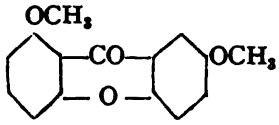


When methylated by means of methyl iodide in the usual manner (v. Kostanecki, Ber., 1894, 27, 1992), euxanthone yields only a *monomethyl ether*, $C_{13}H_7O_2(OCH_3)$, (yellow plates, melting-point 129°), and this on treatment with strong sodium hydroxide solution gives an insoluble yellow sodium salt. The latter, by washing with water, is decomposed with regeneration of the free monomethyl ether. These reactions indicate that euxanthone contains an hydroxyl in the ortho position to a carboxyl group (cf. also Herzig, Monatsh., 12, 161), and that, therefore, its constitution is represented by formula (2). The final proof of this formula is afforded by a later synthesis of euxanthone (Ullmann and Panchaud, Annalen, 350, 108).

2-Chloro-6-methoxybenzoic acid is condensed with the potassium derivative of hydroquinone monomethyl ether, employing copper powder as a catalyst—

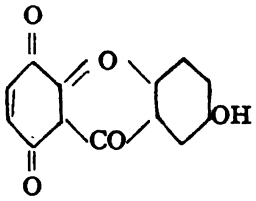


The resulting 4-methoxy-2-phenoxy-6-methoxy-benzoic acid when treated with concentrated sulphuric acid is converted into euxanthone dimethyl ether—

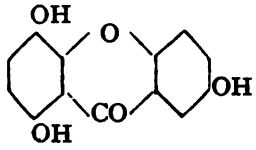


and this by treatment with aluminium chloride in the presence of benzene gives euxanthone.

According to Neirenstein (Ber., 1913, 46, 649) by oxidising euxanthone with chromic acid the quinone



is produced. This consists of dark red needles soluble in alkali with a blue coloration, and on reduction is converted into 2 : 5 : 8 trihydroxy-xanthone, pale yellow needles, melting-point 328—330°.



The triacetyl derivative melts at 226—230°.

Disazobenzene-euxanthone, $C_{13}H_6O_4(C_6H_5N_2)_2$, (Perkin, Chem. Soc. Trans., 73, 666), red needles, melting-point 249—250° (decomp.), is readily prepared by adding diazobenzene sulphate to a weak alkaline solution of euxanthone.

Acetyldisazobenzene-euxanthone, ochre-yellow needles, melts at 197—199°.

Euxanthone possesses only feeble tinctorial properties; the respective shades obtained with woollen cloth mordanted with chromium, aluminium, and tin being dull brown-yellow, pale bright yellow, and very pale bright yellow (Perkin and Hummel, Chem. Soc. Trans., 1896, 69, 1290).

Gentian Root.

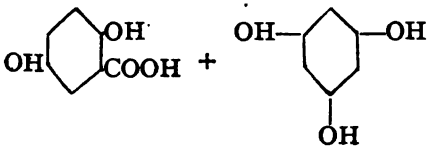
The *Gentiana lutea* (Linn.), from which the gentian root is derived, chiefly occurs in mountainous districts, especially in

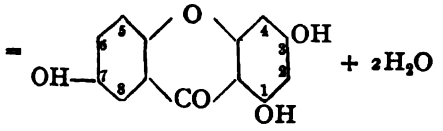
Switzerland and the Tyrol. There is present in the root of this and other species of *gentiana* a bitter principle which is said to possess valuable tonic virtues, and on this account some quantity of the material is imported into this country for medicinal purposes.

Gentisin, the colouring matter of gentian root, was first isolated by Henry and Caventou (J. Pharm. Chim., 1821, 178), and was shown by Baumert (Annalen, 62, 106) to possess the formula $C_{14}H_{10}O_5$. Hlasiwetz and Habermann (*ibid.*, 175, 63; 180, 343), somewhat later, found that gentisin contains two hydroxyl groups, and that, when fused with potassium hydrate, phlorglucinol and gentisic acid (hydroquinone carboxylic acid) are produced from it. By the action of hydrochloric acid on gentisin, methyl chloride was evolved, a probable indication of the presence of a methoxy group. To prepare gentisin (Baumert, *loc. cit.*), the root is well washed with water, then extracted with alcohol, and the extract evaporated to a small bulk. The residue is washed with water to remove the bitter principle, and then with ether to extract plant wax. For purification, the crude colouring matter is repeatedly crystallised from alcohol; 10 kilos. of the root yield about 4 grams of the substance. Gentisin crystallises in yellow needles, is sparingly soluble in alcohol, and dissolves in alkaline solutions with a yellow colour.

Gentisein, $C_{13}H_8O_5$, $2H_2O$.—When gentisin is digested with boiling hydriodic acid, it is converted into gentisein with evolution of 1 molecule of methyl iodide. Gentisein consists of straw-yellow needles, melting at 315°, and gives with sodium amalgam a blood-red coloration, whereas gentisin, by a similar method, yields a deep green coloured liquid (v. Kostanecki, Monatsh., 12, 205). By the action of acetic anhydride, gentisein is converted into the *triacetyl* derivative, $C_{13}H_5O_5(C_2H_3O)_3$, needles, melting-point 226° (v. Kostanecki, *loc. cit.*); but on methylation with methyl iodide, a *dimethyl ether*, $C_{13}H_5O_2(OH)(OCH_3)_2$, yellow needles, melting-point 167°, is produced (v. Kostanecki and Schmidt, Monatsh., 12, 318).

Partial methylation converts gentisein into gentisin, and it is thus certain that the latter consists of *gentisein monomethyl ether*. v. Kostanecki and Tambor (Monatsh., 15, 1) obtained gentisein by distilling a mixture of phloroglucinol and hydroquinone carboxylic acid with acetic anhydride—



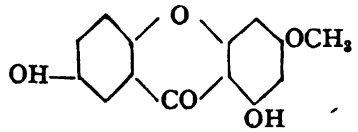


and its constitution is therefore represented as 1 : 3 : 7 *trihydroxyxanthone*. By a study of *disazobenzene-gentisin*, $C_{14}H_8O_5(C_6H_5N_2)_2$, scarlet-red needles, melting-point 251—252° (Perkin, Chem. Soc. Trans., 73, 1028), which gives the *diacetyl* derivative,

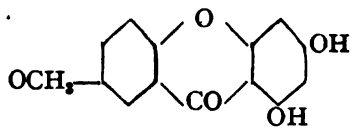
$$C_{14}H_6O_5(C_2H_3O)_2(C_6H_5N_2)_2,$$

orange-red needles, melting-point 218—220°, it has been shown that gentisin itself possesses the constitution (1).

(1)



(2)



As gentisin yields by means of methyl iodide only a monomethyl ether, the original methoxy group cannot be in the position (1). On the other hand, if gentisin is represented by the formula (2), the azobenzene groups would enter the positions 4 and 2, and from such a compound an acetyl derivative cannot be obtained in the ordinary manner (compare disazobenzene phloroglucinol).

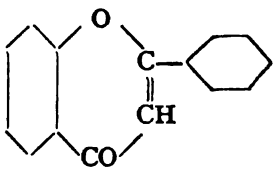
Gentisin is a feeble dyestuff, and gives on wool mordanted with chromium, aluminium, and tin, respectively, pale green-yellow, pale bright yellow, and very pale cream-coloured shades (Perkin and Hummel, Chem. Soc. Trans., 1896, 69, 1290).

CHAPTER V.

FLAVONE GROUP.

Flavone — Natural Flavone — Diflavone—Poplar Buds—Parsley—Chamomile Flowers — *Robinia pseud-acacia* — *Vitex littoralis* — *Saponaria officinalis*— *Lotus arabicus*—Weld—Dyer's Broom—Fukugi—Scoparin—Scutellarein—Coumaranone.

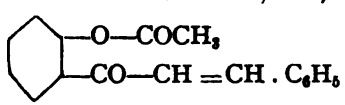
FLAVONE, the mother substance of a large and very important group of natural colouring matters,



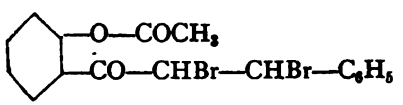
has been synthesised by the following methods:—

(*a*) Acetyl-*o*-hydroxybenzylideneacetophenone (1) yields the dibromide (2) (Feuerstein and v. Kostanecki, Ber., 1898, 36, 1757)—

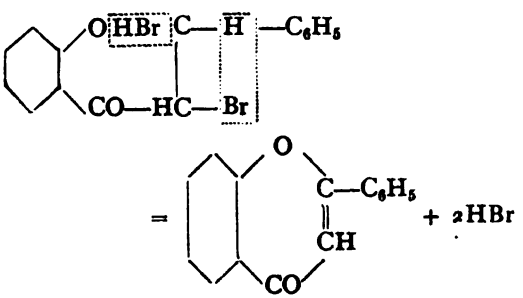
(1)



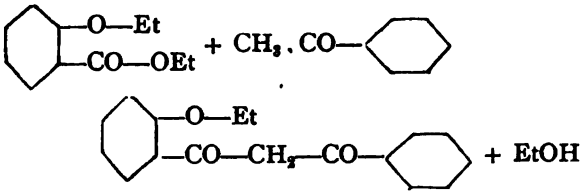
(2)



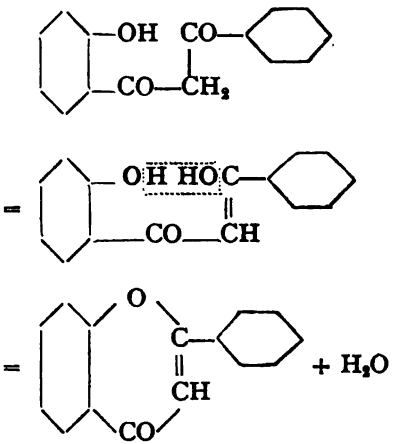
and the latter, on treatment with alcoholic potash, is converted into flavone, according to the following scheme:—



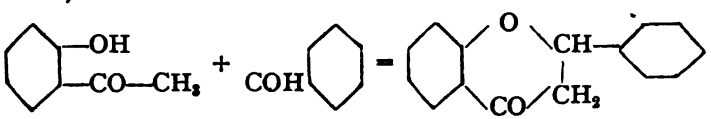
(*b*) Again (v. Kostanecki and Tambor, Ber., 1900, 33, 330), ethyl *o*-ethoxybenzoate and acetophenone, in the presence of sodium, give *o*-ethoxybenzoylacetophenone—



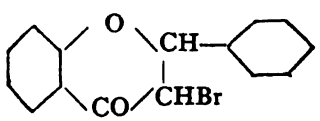
This compound, when digested with boiling hydriodic acid, gives flavone—



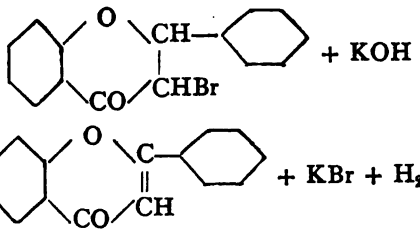
(*c*) Orthohydroxyacetophenone derivatives can be condensed with aromatic aldehydes with production of flavanones (dihydroflavones)—



On treatment with bromine bromflavanone is produced—



and this by means of alkalis splits off hydrobromic acid and is converted into the flavone—

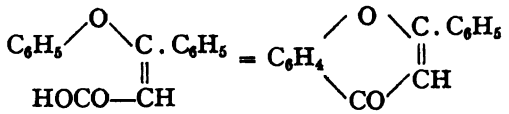


(v. Kostanecki, Levi, and Tambor, Ber., 1899, 32, 326).

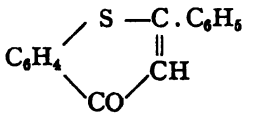
(*d*) More recently Ruhemann (Ber., 36, 1913, 2188) has employed for the synthesis of flavone the esters of β-hydroxyaryl cinnamic acids. These may be prepared by the interaction of phenyl propiolic acid esters with sodium phenolates—

$$C_6H_4 . C : C . COOEt + NaO . C_6H_5 = C_6H_5 . C(OC_6H_5) : CNa . COOEt$$

These esters are readily transformed into the free acids, the chlorides of which by means of aluminium chloride give the corresponding flavones. Thus β-phenoxy cinnamic acid in this way gives flavone—



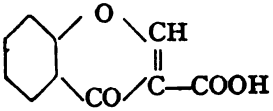
and substituted flavones can be readily prepared by the employment of cinnamic acids containing ether hydroxyaryl nuclei. Phenyl thiocinnamic acid from thiophenol and phenyl propiolic acid ethyl ester, $C_6H_5 . C(SC_6H_5) : CH . COOH$, in this manner yields *thioflavone*—



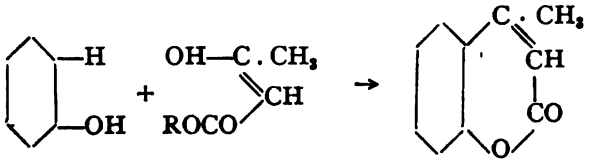
a compound which crystallises in yellow needles and closely resembles flavone.

In case the β-hydroxyaryl cinnamic acids are here replaced by the corresponding derivatives of fumaric acid, benzo γ-pyrone (*chromone*), carboxylic acids are produced which readily evolve carbonic acid gas with formation of chromone. Thus β-phenoxy-fumaric acid, $COOH . C(OC_6H_5) : CH . COOH$, gives benzo-γ-pyrone (chromone) carboxylic acid—*

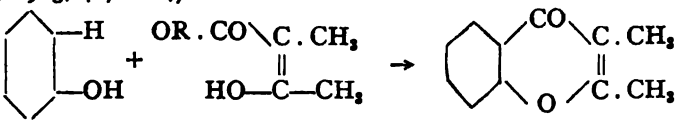
* Though chromone itself was first obtained by Ruhemann and Stapleton (*loc. cit.*), chromone derivatives had been prepared slightly earlier by v. Kostanecki (Ber., 1900, 1998), who employed for this purpose methods similar to those he had found serviceable for the synthesis of flavone compounds.



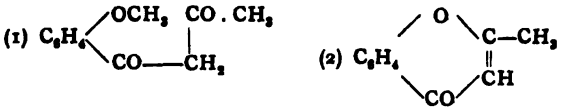
(*e*) Simonis (Ber., 1914, 47, 2229), again, has described another method for the synthesis of flavone. Whereas Pechmann and Duisberg found that phenols could be condensed by means of sulphuric acid with the esters of β-ketonic acids, to form *a*-pyrone (coumarin) derivatives, according to the following equation which illustrates the preparation of methyl-coumarin from phenol and acetoacetic ether



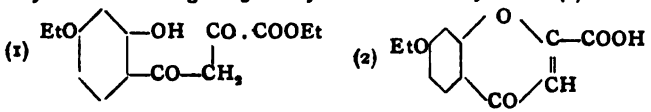
by employing phosphorus pentoxide as the condensing agent the reaction takes another course. Thus phenol and methylaceto-acetic ether in this way gives dimethyl-chromone (Petschek and Simonis, Ber., 1913, 46, 2014)—



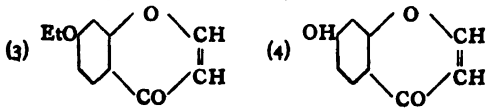
Thus the diketone (1), (compare method (*c*) above) obtained by the interaction of *o*-methoxy-benzoic acid methyl ester, and acetone on treatment with hydriodic acid, gives β-methyl-chromone (2)—



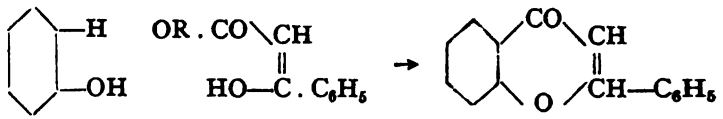
Again, according to v. Kostanecki, Paul, and Tambor, the diketone (1) prepared from resacetophenone monoethyl ether and ethyl oxalate, on treatment with alcoholic hydrochloric acid gives 3 ethoxychromone carboxylic acid (2)—



This when melted gives 3 ethyoxychromone (3), and by means of hydriodic acid can be converted into 3 hydroxychromone (4)—



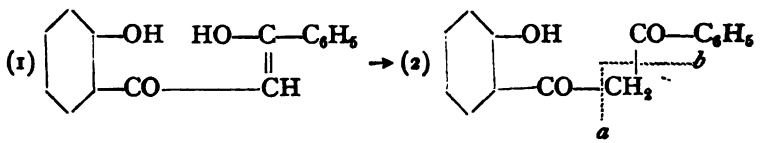
whereas benzoy-lacetic ether and phenol (*ibid.*, 1914, 46, 2232) give flavone



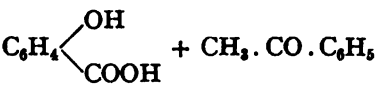
Flavone crystallises from ligroin in colourless needles, melting-point 97°, and is readily soluble in the usual organic solvents. Its solution in sulphuric acid is yellow and possesses a weak blue fluorescence.

By the action of alkalis, flavone and hydroxyflavones suffer hydrolysis according to the following scheme:—

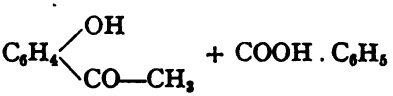
The first product of the reaction owing to the disruption of the pyrone ring is the β-diketone (2)—



and this change may be regarded as the reverse of its synthesis according to method (*b*). The ketone then suffers further hydrolysis as shown by the dotted lines (*a*) into acetophenone and salicylic acid—



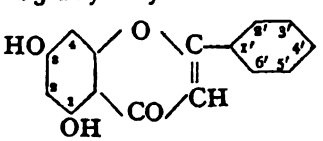
or (*b*) *o*-hydroxy acetophenone and benzoic acid—



The products of the hydrolysis of naturally occurring flavone colouring matters have in the past been mainly instrumental in determining their constitution.

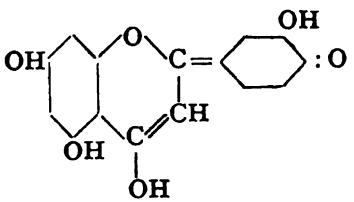
All natural hydroxyflavones which have at present been carefully examined dye aluminium mordanted fabrics a yellow shade, the intensity of which is dependent upon the position of their hydroxyl groups.

Thus chrysin 1 : 3 dihydroxyflavone



and apigenin 1 : 3 : 4′ trihydroxy flavone possess but feeble dyeing property,* whereas luteolin 1 : 3 : 3′ : 4′ tetrahydroxy flavone is a strong colouring matter. Though Liebermann and v. Kostanecki's rule is in this instance but partially applicable, it is evident that the dyeing property in the flavone group is only fully developed when at least two hydroxyls in the ortho position to one another are present. There is every reason to anticipate also that a 3 : 4 dihydroxy-flavone would, like luteolin, possess well-marked dyeing properties, and indeed such an arrangement may be present in scutellarein. Of the influence, however, of such a grouping in the positions 2′ : 3′ : 2 : 3 and 1 : 2, information is at present lacking, as compounds possessing these characteristics have as yet to be discovered.

According to the quinonoid theory, it has been suggested that the flavone colouring matters, at least in the form of their lakes, may possess a paraquinonoid structure, which in the case of luteolin may be represented thus—

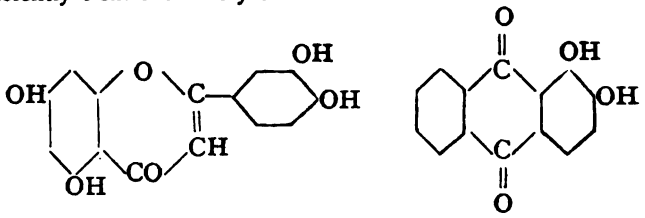


and such a formula has been applied by Perkin (Chem. Soc. Trans., 75, 433) to the monoalkali and oxonium salts of these compounds. A discussion of the quinonoid theory of colour, about which there is considerable diversity of opinion among chemists, hardly enters into the scope of this volume,† though the theory advanced by Watson (Chem. Soc. Trans., 1914, 105, 759) may be recorded here, in that it suggests an explanation of the lack of depth of colour possessed by the flavone dyes in comparison with those of the anthraquinone group, red, violet, blue, black, and brown being for instance deeper than orange and yellow. It is pointed out by Watson that dyes which are quinonoid in all possible tautomeric forms exhibit a deep colour, the opposite being generally the case with those which cannot be represented in this way. Numerous instances are cited to

* The shades given by these and other feeble colouring matters of a similar type can be more satisfactorily observed by employing mordanted wool rather than mordanted calico.

† For a discussion of this and other theories concerning the influence of constitution on colour, see Professor Watson's "Colour in Relation to Chemical Constitution" in this series of monographs.

illustrate this point, for which the paper itself should be consulted, but an examination of the formula of luteolin and alizarin will render sufficiently clear the theory of this author—



Luteolin, the only flavone colouring matter possessing strong dyeing property which has been carefully examined, gives shades possessing considerable fastness to light, and these are much more permanent than those given by the present known members of the flavonol group.

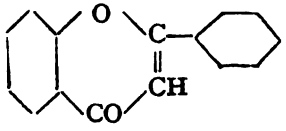
Natural Flavone.

Very interesting is the occurrence of flavone in nature (Müller, Chem. Soc. Trans., 1915, 107, 872). It is well known that many varieties of the primula possess on their flower stalks, leaves, and seed capsules a characteristic dust termed by gardeners "meal" or "farina," and this is most pronounced on varieties recently obtained from China and Japan. This powder, examined by Hugo Müller who obtained it mainly from the *P. pulverulenta* and *P. japonica*, dissolves readily in benzene and boiling ligroin, and the concentrated solution on cooling became semi-solid owing to the separation of crystalline tufts.

It possessed the formula $C_{15}H_{10}O_2$, melted at 99—100°, and on boiling with dilute sodium hydroxide gave slowly a yellow solution, with formation of a small quantity of acetophenone, and the latter could be obtained in greater quantity by the action of methyl alcoholic sodium hydroxide. Employing methyl alcoholic barium hydroxide, a reagent not previously suggested for the degradation of flavone compounds, Müller obtained a substance $C_{15}H_{12}O_3$. This by the action of alkalis was converted into salicylic acid and acetophenone and evidently consisted of hydroxy-benzoyl-acetophenone (*o*-hydroxy-dibenzoyl-methane)—

$$OH . C_6H_4 . CO . CH_2 . CO . C_6H_5$$

The compound $C_{15}H_{10}O_2$ was thus without doubt *flavone*, and

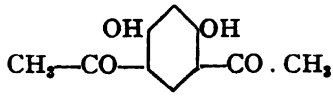


it is interesting to note that though hydroxybenzoyl-acetophenone was assumed by Feuerstein and v. Kostanecki (Ber., 1898, 31, 1758) to be the first product of the hydrolysis of this substance, its isolation in this manner had not previously been effected.

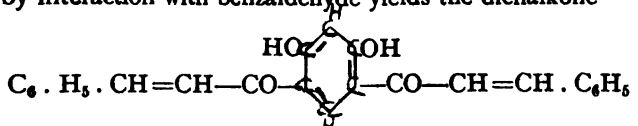
The function which flavone exercises in the economy of the plant life of the primula is difficult to explain, though it may be of service on account of its repellent action towards water.

Diflavone.

This substance was prepared by Ryan and O'Neill (Proceedings Royal Irish Academy, xxxii., B, 5, 48), who employed as a starting-point for their synthesis diacetoresorcinol—



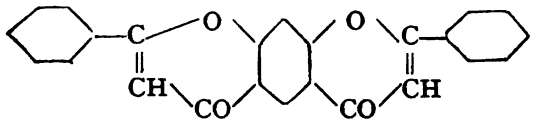
This by interaction with benzaldehyde yields the dichalkone



the acetyl compound of which when brominated forms the tetra-bromide

$$C_6H_5(O \cdot COCH_3)_2\,(CO \cdot CHBr \cdot CH \cdot Br \cdot C_6H_5)_2$$

Alcoholic potash converts the latter compound into *diflavone*—



and this crystallises in faint yellow needles, melting-point 277—278°. In its general properties diflavone resembles flavone, and its faint yellow solution in sulphuric acid has a beautiful blue fluorescence. Colouring matters of this group are at present unknown.

Poplar Buds.

Chrysin, $C_{15}H_{10}O_4$, is contained in the leaf buds of the poplar (*Populus pyramidalis*, Salisb., *P. nigra*, Linn., *P. monilifera*, Ait.), in which it is present to the extent of about ½ per cent. It was first isolated by Piccard (Ber., 6, 884, 1160; 7, 888; 10, 176) and is best prepared by the method devised by this chemist.

An alcoholic extract of 1000 grams of poplar buds is treated while hot with about 120 grams of lead acetate, and after standing for some

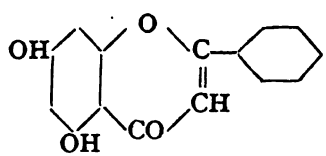
time the yellow precipitate is removed. Through the clear filtrate sulphuretted hydrogen is passed in order to decompose lead salts, the sulphide of lead is filtered off and the liquid evaporated to dryness. The residue dissolved in a little hot alcohol gradually deposits crystals of chrysin, which are collected, successively extracted with carbon disulphide, benzene, and boiling water, and finally crystallised two or three times from alcohol.

Pure chrysin crystallises in colourless leaflets, melting-point 275°, and dissolves in alkaline solutions with an intense yellow coloration. When acetylated, *diacetylchrysin*, $C_{15}H_8O_4(C_2H_3O)_2$, colourless needles, melting-point 185°, is produced, but by the action of methyl iodide in the usual manner a *monomethylether*, $C_{15}H_9O_3 . OCH_3$, melting-point 163°, only can be prepared. The latter yields *acetylchrysin-monomethylether*, $C_{15}H_8O_3(OCH_3)C_2H_3O$, colourless needles, melting-point 149°, and with alcoholic soda gives a bright yellow sodium salt which is decomposed by washing with water (v. Kostanecki, Ber., 1893, 26, 2901).

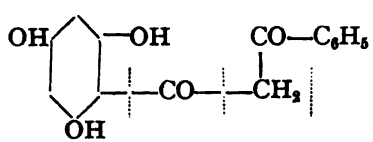
When digested with boiling concentrated potassium hydroxide solution, chrysin gives *phloroglucinol*, *benzoic acid*, *acetic acid*, and *acetophenone* (Piccard, *loc. cit.*), the last-named in very small quantity, and the reaction can be expressed as follows :—

$$C_{15}H_{10}O_4 + 3H_2O = C_6H_6O_3 + C_6H_5 . COOH + CH_3 . COOH$$

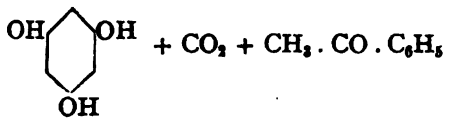
The investigations of v. Kostanecki (*loc. cit.*) indicate that chrysin is a *dihydroxyflavone* and possesses the constitution—



The first hypothetical product of the hydrolysis of chrysin by means of alkali (cf. flavone) is 2 : 4 : 6-trihydroxybenzoylacetophenone—

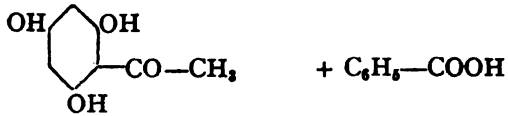


which subsequently yields *phloroglucinol*, *acetophenone*, and *carbon dioxide*—



Phloroglucinol. Acetophenone.

On the other hand, *phloracetophenone* (which is unstable in the presence of alkali and is thereby converted into phloroglucinol and acetic acid) and benzoic acid are also produced—

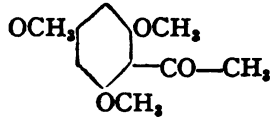


Phloracetophenone. Benzoic acid.

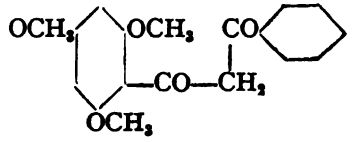
Chrysin has been synthesised by Emilewicz, v. Kostanecki, and Tambor (Ber., 32, 2448) in the following manner :—

Phloroacetophenonetrimethylether (1) gives, when treated with ethyl benzoate in the presence of sodium, 2 : 4 : 6-trimethoxybenzoylacetophenone (2)—

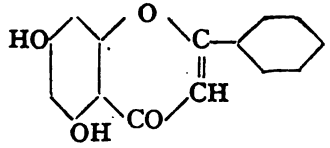
(1)



(2)



(3)



The latter, when digested with strong boiling hydriodic acid, is demethylated and ring formation occurs with the production of chrysin (3).

The following derivatives of chrysin have been prepared :—

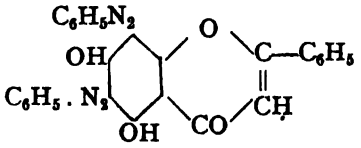
Dibromchrysin, $C_{15}H_8Br_2O_4$ (Piccard, Ber., 1873, 6, 886); *Diiodochrysin*, $C_{15}H_8I_2O_4$, yellow needles (Piccard); *Dinitrochrysin*, $C_{15}H_8(NO_2)_2O_4$, red leaflets, melting-point 272° (Piccard and Darier,

Ber., 1894, 27, 21); *Chrysin monoethylether*, $C_{15}H_9O_3(OC_2H)_5$, thin needles, melting-point 146° (Piccard); *Chrysinisoamylether*,

$$C_{15}H_9O_3(OC_5H_{11}),$$

thin needles, melting-point 125° (Piccard); *Dibromchrysin isoamyl ether*, $C_{15}H_7Br_2O_2(OC_5H_{11})$, needles; and *Dinitro-diacetylchrysin*, $C_{15}H_6O_4(NO_2)_2(C_2H_3O)_2$, yellow needles, melting-point 229° (Darier, *loc. cit.*).

Disazobenzenechrysin (Perkin, Chem. Soc. Trans., 1896, 69, 1439)—



orange-red needles, melting-point 251—252°, insoluble in alkaline solutions, is unaltered by prolonged digestion with acetic anhydride.

Chrysin is a feeble dyestuff. The shades produced on wool mordanted with aluminium, chromium, and iron, are respectively pale bright yellow, pale yellow-orange, and chocolate-brown.

Tectochrysin, a second constituent of poplar buds, is present in the benzene extracts from the crude chrysin. Tectochrysin is *chrysin monomethylether*, ($C_{15}H_9O_3 . OCH_3$), (Piccard), and is identical with the methylation product of chrysin itself (*loc. cit.*).

Parsley.

Apiin, the glucoside of apigenin, is found in the leaves, stem, and seeds of parsley (*Carum* (*Apium*) *petroselinum*, Benth. and Hook.), (Rump, Buchner's Repert. f. Pharm., 1836, 6, 6; Braconnot, Ann. Chim. Phys., 1843, iii., 9, 250). Both authors obtained it as a gelatinous mass by extracting parsley seeds with boiling water, and considering the readiness with which it gelatinised, Braconnot included it among the members of the pectin class. Subsequently, Planta and Wallace assigned to it the formula $C_{24}H_{28}O_{18}$ (Annalen, 1850, 74, 262), and though by the action of boiling dilute acids a brown substance, $C_{24}H_{20}O_9$, was produced, it did not appear that apiin was a glucoside. On the other hand, Lindenhorn (Inaugural Dissert. Wurzburg, 1867), who obtained this substance in a crystalline condition, found that by the action of dilute acids it was decomposed into glucose and apigenin, and that the reaction probably proceeded as follows:—

$$C_{12}H_{14}O_7 + H_2O = C_6H_4O_2 + C_6H_{12}O_6$$

Von Gerichten (Ber., 1876, 9, 1124), who found for apiin and apigenin numbers identical with those given by Lindenhorn, showed that on fusion with alkali apiin gave *phloroglucinol* and an acid not closely examined, but which, by the further action of the alkali, gave *protocatechuic acid* besides some *oxalic, formic*, and *para-hydroxybenzoic acids*. As a result of his investigation, von Gerichten considered the most probable formula for apigenin to be $C_{15}H_{10}O_5$, and that the decomposition of the glucoside apiin with acids might be represented as follows :—

$$C_{27}H_{32}O_{16} + H_2O = 2C_6H_{12}O_6 + C_{15}H_{10}O_5$$

In a later communication (Annalen, 318, 124), however, he adopted the formula $C_{26}H_{28}O_{14} . H_2O$, as he found that on hydrolysing apiin with ½ per cent. sulphuric acid it is converted into *apiose* and *glucose apigenin*—

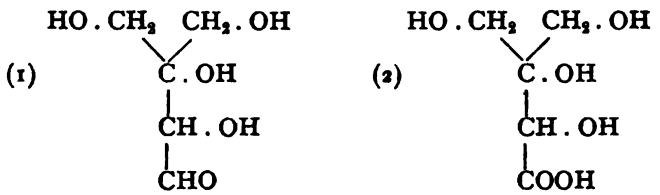
$$C_{26}H_{28}O_{14} + H_2O = \underset{\text{Apiose.}}{C_5H_{10}O_5} + \underset{\text{Glucose apigenin.}}{C_6H_{11}O_6 . C_{15}H_9O_4}$$

By the prolonged action of the acid, the latter compound gives apigenin and glucose—

$$C_6H_{11}O_6 . C_{15}H_9O_4 + H_2O = C_6H_{12}O_6 + C_{15}H_{10}O_5$$

Apiin therefore contains a disaccharose nucleus which on hydrolysis yields dextrose and apiose.

Apiose is an aldopentose of the formula (1), and on oxidation gives *apionic acid* (2)—



By the action of hydriodic acid and phosphorus, apionic acid is reduced to *iso*-valeric acid.

When apiin is boiled with nitric acid in 60 per cent. acetic acid it is converted into the nitromonoglucoside *nitroapigetrin*, $C_{21}H_{21}O_{11}NO_2$, a yellow crystalline powder, melting-point 254—255°, soluble in alkaline solutions with a yellow colour (Perkin, Chem. Soc. Trans., 1900, 416, 77).

Apiin forms colourless needles, melting-point 228°, easily soluble in hot water and alcohol. From these solutions it separates on cooling in the gelatinous condition.

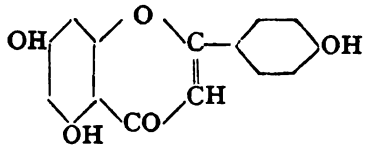
Whereas apiin can be most readily obtained in a pure condition from the seeds of parsley, it has been shown by von Gerichten that the stem and leaves of this plant contain in addition a glucoside of a *luteolin monomethylether*. By fusion with alkali, pure apigenin gives phloroglucinol and p-*hydroxybenzoic acid* (Ber., 1900, 33, 2334). The previous isolation of *protocatechuic acid*, according to this method by von Gerichten, and Perkin (Chem. Soc. Trans., 1897, 71, 805), was due to its contamination with a trace of this luteolin derivative.

In order to prepare apigenin, Perkin (*loc. cit.*) digests 30 grams of apiin for twenty hours with 3 litres of hydrochloric acid (sp. gr. 1·04). The crude colouring matter is extracted with boiling alcohol, and the extract treated with alcoholic lead acetate solution, drop by drop, until the supernatant liquid becomes colourless. The lead precipitate is then removed, and the filtrate after treatment with a few drops of acetic acid is evaporated to a small bulk. By addition of a little boiling water and gentle evaporation, the apigenin separates in a crystalline condition.

Should the substance be contaminated with luteolin monomethylether, it is digested for two hours with boiling hydriodic acid (sp. gr. 1·96) and the product crystallised from alcohol. The more soluble luteolin thus formed remains in solution (Czajkowski, v. Kostanecki, and Tambor, Ber., 1900, 33, 1996).

Apigenin thus prepared crystallises in almost colourless leaflets, melting-point 343°, and dissolves in alkaline solutions with a yellow coloration. By means of acetic anhydride *triacetyl-apigenin*, colourless needles, melting-point 181—182°, is produced (Czajkowski, v. Kostanecki, and Tambor), but when methylated by means of methyl iodide, only a *dimethylether*, $C_{15}H_8O_3(OCH_3)_2$, pale yellow needles, melting-point 171—172° (Perkin, *loc. cit.*), can be prepared. On acetylation this yields *acetylapigenin dimethylether*, colourless needles, melting-point 195—196° (Perkin), and by means of alcoholic potash is transformed into a yellow potassium salt which is decomposed by washing with water. When hydrolysed with alcoholic potash, apigenin dimethylether yields *anisic acid* and a syrupy phenolic substance, which probably contains *phloroglucinol monomethylether*.

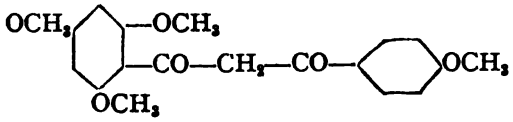
If apigenin is digested with 50 per cent. potassium hydroxide solution, it is hydrolysed with formation of p-*hydroxyacetophenone* and phloroglucinol (Perkin, *loc. cit.*). From the result of his investigation, Perkin assigned to apigenin the constitution of a *hydroxychrysin*, or 1 : 3 : 4′ : *trihydroxyflavone*—



Somewhat later, Czajkowski, v. Kostanecki, and Tambor (*loc. cit.*) synthesised apigenin by a series of reactions similar to those employed for the preparation of chrysin (Emilewicz, v. Kostanecki, and Tambor, Ber., 32, 2448).

Phloracetophenone trimethylether condensed with *ethyl anisate* in the presence of sodium gives *tetramethoxybenzoylacetophenone* (1), and this on boiling with hydriodic acid is converted into apigenin (2)—

(1)



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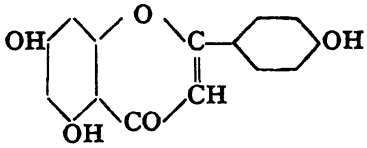
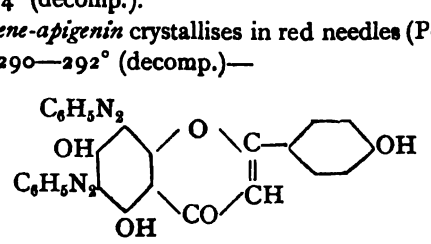


The following derivatives of apigenin have been prepared:—

Apigenin diethylether, $C_{15}H_8O_3(OC_2H_5)_2$, yellow needles, melting-point 161—162° (Perkin), 163—164° (Czajkowski, v. Kostanecki, and Tambor); *acetylapigenin diethylether*, $C_{15}H_7O_3(OC_2H_5)_2 . C_2H_3O$, colourless needles, melting-point 151—152° (Perkin), 148—149·5° (Czajkowski, v. Kostanecki, and Tambor); *tribenzoylapigenin*, $C_{15}H_7O_5(C_7H_5O)_3$, colourless needles, melting-point 210—212° (Perkin); *dibromapigenin*, $C_{15}H_8Br_2O_5$, pale yellow needles; *mononitroapigenin*, $C_{15}H_9O_5(NO_2)$, orange-yellow prismatic needles; *trinitroapigenin*, $C_{15}H_7O_5(NO_2)_3$, minute yellow needles; and *tetranitroapigenin*, $C_{15}H_6O_5(NO_2)_4$, almost colourless needles, melting-point 243—244° (decomp.).

Disazobenzene-apigenin crystallises in red needles (Perkin, *loc. cit.*), melting-point 290—292° (decomp.)—



and with acetic anhydride gives only the monoacetyl-derivative, $C_{15}H_7O_5(C_2H_3O)(C_6H_5N_2)_2$, orange-red needles, which commence to decompose at 260° and melt at about 277—280°.

Apigenin closely resembles chrysin in its tinctorial properties, although it is a somewhat stronger dyestuff. The shades it gives upon wool mordanted with aluminium, chromium, and iron are respectively pure yellow, weak yellow-orange, and chocolate-brown.

Apigenin is also present in weld (*Reseda luteola*), (Perkin and Horsfall, Chem. Soc. Trans., 1900, 77, 1314), in the flowers of *Antirrhinum majus* (Wheldale and Bassett, Biochem. Jour., 1913, 7, 441), and exists probably also in chamomile flowers (Perkin).

Chamomile Flowers.

Anthemis Nobilis.—An examination of the flowers of *Anthemis nobilis* (Linn.) by Power and Browning (Chem. Soc. Trans., 1914, 105, 1833) has shown that these contain in addition to numerous other substances an *apigenin glucoside*, $C_{21}H_{20}O_{10}.2H_2O$, faintly yellow microscopic crystals melting at 178—180°. It dissolves in alkalis with a yellow colour and gives with aqueous ferric chloride a purplish-brown coloration. Dried at 125—130° it loses one molecule of water of crystallisation, but the second molecule cannot be eliminated without decomposing the substance. This is evident from the composition of the *hexa-acetyl* derivative, $C_{21}H_{14}O_{10}(COCH_3)_6$, colourless microscopic crystals, melting-point 144—146°, the molecule of water in question being eliminated in the process of acetylation.

By digestion with 5 per cent. aqueous sulphuric acid for three hours, this glucoside yields apigenin and dextrose according to the equation—

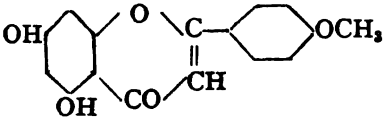
$$C_{21}H_{20}O_{10}, H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_6$$

Robinia pseud-acacia.

Acacetin, $C_{16}H_{12}O_5$, the colouring matter of the leaves of the *Robinia pseud-acacia* (Linn.) (common or false acacia, North American locust), forms almost colourless needles, soluble in alkalis with a pale yellow coloration (Perkin, Chem. Soc. Trans., 1900, 71, 430).

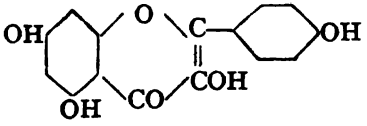
To prepare it a boiling aqueous decoction of the leaves is treated with basic lead acetate solution, and the pale yellow precipitate is suspended in water and decomposed with boiling dilute sulphuric acid. From the clear liquid the colouring matter is removed by extraction with ether and purified by crystallisation from dilute alcohol.

Acacetin forms a *diacetyl derivative*, $C_{16}H_{10}O_5(C_2H_3O)_2$, colourless needles, melting-point 195—198°, and when fused with alkali gives phloroglucinol and *p*-hydroxybenzoic acid. Digested with boiling hydriodic acid it yields apigenin and one molecule of methyl iodide, and is consequently an *apigenin monomethylether*. Acacetin is very probably identical with von Gerichten's apigenin methyl ether (Ber., 1900, 33, 2908)—



the acetyl derivative of which melts at 198—200°.

Interesting is the fact that the flowers of the *Robinia pseud-acacia* contain *robinin*, a glucoside of the trihydroxy flavonol kaempferol—



which contains one more hydroxyl than apigenin. This is referred to later.

VITEXIN.

The *Vitex littoralis* (A. Cunn.) or "Puriri" is a large tree, 40—60 feet high, and 3—5 feet in diameter, which grows only in the northern portion of the North Island of New Zealand. The wood affords a very durable timber, and is chiefly used for house blocks, fencing posts, piles for bridges, railway sleepers, etc.

Vitexin, the main colouring matter, is present in the wood in the form of a glucoside which has not yet been isolated. It is prepared by digesting a purified extract of the dyestuff with boiling dilute hydrochloric acid, and by this means separates in the form of a yellow viscous mass. By extracting this crude product with boiling alcohol, a pale yellow crystalline powder remains undissolved, and this, owing to its sparing solubility, is most readily purified by acetylation, and the subsequent hydrolysis of the pure acetyl derivative (Perkin, Chem. Soc. Trans., 1898, 74, 1020).

Vitexin consists of minute canary-yellow prismatic or fine hair-like needles, soluble in alkaline solutions with a pale yellow coloration, and from these solutions when boiled it is deposited by acidification in a crystalline condition.

On fusion with alkali vitexin yields *phloroglucinol* and *p-hydroxybenzoic acid*, and when digested with boiling 50 per cent. potassium

hydroxide solution *p-hydroxyacetophenone* is also produced. Boiling 15 per cent. nitric acid gives dinitro-*p*-hydroxybenzoic acid, together with a small quantity of *tetranitroapigenin*, melting-point 239—241°. The formula first assigned to vitexin by Perkin was $C_{15}H_{14}O_7$, and the *acetyl derivative*, colourless prismatic needles, melting-point 251—256°, was consequently represented as $C_{15}H_9O_7(C_2H_3O)_5$. In a later communication in view of its apparent relationship to apigenin, and the difficulty of accounting for the large number of hydroxyl groups which are present, it is suggested by this author (Chem. Soc. Trans., 1899, 77, 422) that vitexin is probably a very stable glucoside of apigenin represented by the formula $C_{21}H_{20}O_{10}$. Vitexin is a somewhat feeble colouring matter, and dyes shades similar to those given by apigenin; these, employing woollen cloth mordanted with chromium, aluminium, and tin, are respectively greenish-yellow, pale bright yellow, and pale brown.

In addition to vitexin the wood of the *Vitex littoralis* contains (as glucoside) a small quantity of a second colouring matter, *homovitexin*. It was obtained as a pale yellow powder, melting-point 245—246°, and is distinguished from vitexin by its ready solubility in alcohol. Fused with alkali it gives phloroglucinol and *p*-hydroxybenzoic acid, and is possessed of feeble dyeing property. The analytical figures approximate to $C_{16}H_{16}O_7$ or $C_{18}H_{18}O_8$.

According to Barger (Chem. Soc. Trans., 1906, 89, 1120) the glucoside saponarin, which is present in *Saponaria officinalis* (Linn.), yields on hydrolysis glucose, saponaretin, and a small quantity of vitexin. It is possible that saponaretin and homovitexin are identical.

SAPONARIA OFFICINALIS (Linn.).

The epidermal cells of the leaves of certain flowering plants contain, dissolved in their cell sap, a substance which is coloured blue by iodine. The colour disappears on warming and returns on cooling, as is the case with starch. On this account the compound was regarded as an amorphous variety of starch by Sanio, its discoverer (Botanische Zeitung, 1857, 15, 420). Schenck (*ibid.*, 1857, 15, 497, 455) doubted whether this substance was identical with starch, and the correctness of this view was confirmed by Nägeli (Beiträge zur wissensch. Botanik, 1860, 2, 187). For the chemical examination of this substance the dried shoots of the *S. officinalis* were selected by Barger (Chem. Soc. Trans., 1906, 89, 1210) as the raw material, because this plant is relatively rich in the compound, and is grown on the Continent for pharmaceutical purposes, so that large quantities are easily obtainable.

Saponarin, $C_{21}H_{24}O_{12}$, $2H_2O$.—The material was extracted with from 10 to 20 times its weight of water for half an hour, and the operation repeated several times. The extracts, strained through linen and concentrated to a quarter their volume, were acidified with acetic acid and left to stand for several weeks. The grey deposit which had then separated was dissolved in hot 1 per cent. sodium carbonate solution (1 litre per kilo. of dry leaves), and after addition of acetic acid was treated with lead acetate, in order to precipitate gums and other impurities. On standing for several weeks the clear liquid deposited crude saponarin, which, however, still contained 30 per cent. of impurity.

The crude saponarin was dissolved in boiling pyridine, the dark brown solution was filtered and evaporated in a vacuum on the water-bath. The residual syrup dissolved in hot water was diluted and on standing deposited the substance in microscopic needles.

Saponarin dried in air is a white powder, but after being dried in a vacuum becomes pale yellow, and is soluble in dilute alkaline solutions with an intense yellow colour. When heated slowly it melts and decomposes at 231—232°, but if the bath is previously heated to 230°, the melting-point is 236°.

On acidifying an alkaline solution, and on diluting a solution in concentrated acids with water, the glucoside is not immediately precipitated if the solution is dilute. This power of remaining in a state of pseudo solution is characteristic of saponarin, and in this condition it gives with iodine in potassium iodide the blue or violet coloration which led to its discovery. This coloration disappears on warming, but returns again on cooling. Saponarin gives with sulphuric acid a blue fluorescent solution.

Ennea-acetyl saponarin, $C_{21}H_{15}O_{12}(C_2H_3O)_9$, microscopic curved needles, melts at 183—185°. It does not give a blue coloration with iodine. When saponarin is boiled with dilute mineral acids, it is slowly hydrolysed according to the equation

$$C_{21}H_{24}O_{12} + H_2O = C_{15}H_{14}O_7 + C_6H_{12}O_6$$

with formation of glucose, *saponaretin* and a small quantity of *vitexin* identical with that obtained by Perkin (Chem. Soc. Trans., 1898, 73, 1030) from *Vitex littoralis* (A. Cunn.). According to Barger, vitexin forms pale yellow glistening plates, melting-point 260°, whereas it is described by Perkin as canary-yellow needles, melting-point 264—265°. Molecular weight determinations carried out by the microscopic method (Barger, Chem. Soc. Trans., 1904, 85, 286; 1905, 87, 1756) indicate that the original formula $C_{15}H_{14}O_7$ assigned

by Perkin to vitexin is correct (*loc. cit.*), rather than the second, $C_{21}H_{20}O_{10}$, which he subsequently proposed.

Saponaretin, $C_{15}H_{14}O_7$?, the chief product of the hydrolysis of saponarin with dilute acid, consists of a light yellow amorphous powder, extremely soluble in alcohol, though in other respects it closely resembles vitexin. It may be that saponaretin is identical with Perkin's homovitexin (*loc. cit.*), which in the case of the *Vitex littoralis* appears to be the minor product of the hydrolysis of the glucoside there present.

Lotus arabicus.

The *L. arabicus* (Linn.) is a leguminous plant, indigenous to Egypt and Northern Africa, and in the young condition is extremely poisonous. It has been investigated by Dunstan and Henry (Phil. Trans., 1901, 194, 515).

Lotusin, the active principle, can be isolated by extracting the dried plant with methyl alcohol. The extract is evaporated, the residue treated with water to remove chlorophyll and resin, and from the aqueous solution tannin and other impurities are precipitated by means of lead acetate. The filtrate, on evaporation, leaves a syrupy residue, from which crystals of lotusin slowly separate. In the pure condition lotusin, $C_{28}H_{31}NO_{16}$, forms yellow needles, and when hydrolysed by digestion with hydrochloric acid, or by means of an enzyme *lotase*, also found in the plant, yields dextrose, *lotoflavin*, and hydrocyanic acid, according to the following equation:—

$$C_{28}H_{31}O_{16}N + 2H_2O = 2C_6H_{12}O_6 + C_{15}H_{10}O_6 + HCN$$

When warmed with alcoholic potash (20 per cent.) lotusin is gradually decomposed with production of ammonia and *lotusinic acid*:—

$$C_{28}H_{31}O_{16}N + 2H_2O = C_{28}H_{32}O_{18} + NH_3$$

Lotusinic acid.

This compound is monobasic, gives yellow crystalline salts, and is hydrolysed by dilute hydrochloric acid with formation of *lotoflavin* *dextrose* and *heptogluconic acid*:—

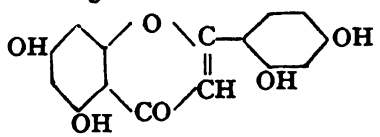
$$C_{28}H_{32}O_{18} + 2H_2O = C_{15}H_{10}O_6 + C_6H_{12}O_6 + C_7H_{14}O_8$$

Lotoflavin, $C_{15}H_{10}O_6$, crystallises in yellow needles, soluble in alkaline solutions with a yellow colour. By fusion with alkali, *phloroglucinol* and *β-resorcylic acid* are produced.

With acetic anhydride lotoflavin gives a *tetra-acetyl* compound, $C_{15}H_6O_6(C_2H_3O)_4$, colourless needles, melting-point 176—178°, and when methylated by means of methyl iodide the *trimethyl ether*, $C_{15}H_7O_3(OCH_3)_3$, is obtained. This latter compound exists in two

forms, viz. the α-form yellow rosettes, melting-point 125°, and the β-form glistening needles, melting-point 175°, which are mutually convertible. Both varieties give by means of acetic anhydride the same *monoacetyl-lotoflavin trimethyl ether*, $C_{15}H_6O_5(C_2H_3O)(OCH_3)_3$, yellow needles, melting-point 147°.

According to Dunstan and Henry, lotoflavin is probably a *tetrahydroxyflavone*, possessing the formula—

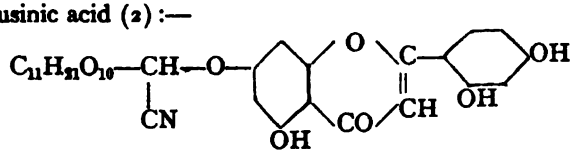


The hydrolysis of the cyanogenetic glucoside lotusin, with formation of maltose, lotoflavin and hydrocyanic acid, may be expressed by the equation—

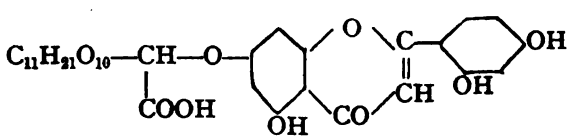
$$C_{28}H_{31}NO_{16} + H_2O = C_{12}H_{22}O_{11} + C_{15}H_{10}O_6 + HCN$$

The following constitutions are respectively assigned to lotusin (1) and lotusinic acid (2):—

(1)



(2)



WELD.

Weld is the dried herbaceous plant known as *Reseda luteola* formerly cultivated to a considerable extent in France, Germany, and Austria. Its cultivation in this country has nearly ceased, because not only is the quantity of colouring matter it contains very small, but the carriage of the plant, owing to its bulky nature, is expensive. A special interest, however, attaches to weld, for it is said to be the oldest European dyestuff known, and was used by the Gauls and other nations dwelling north of the Alps in the time of Julius Cæsar.

The plant attains a height of about 3 feet, is pale brown in colour, and is sold in sheaves like straw. The colouring matter is disseminated throughout the entire plant, but the greater quantity occurs in the upper extremity and the seeds.

Luteolin, the main colouring matter of weld, was examined by Chevreul (J. Chim. Med., 6, 157; Annalen, 82, 53), who obtained it in a crude condition; its isolation in a state of chemical purity was first achieved by Moldenhauer (Annalen, 100, 180), who assigned to it the formula $C_{30}H_{14}O_8$. It was subsequently investigated by Schützenberger and Paraf (Bull. Soc. Chim., 1861, (i.), 18), who proposed the formula $C_{12}H_8O_5$ and purified it in a somewhat novel manner which is worthy of mention. Weld was exhausted with alcohol, the extract evaporated, and treated with water, which threw down a dirty greenish precipitate. This was collected, introduced with a little water into a sealed tube and heated to 250°. On cooling the sides of the tube were found to be coated with golden-yellow needles of luteolin, and the impurities had collected at the bottom of the tube to form a resinous cake.

Hlasiwetz suggested that luteolin had the formula $C_{15}H_{10}O_6$ and was isomeric with the paradiscetin, which he obtained during the fusion of quercetin with alkali (Annalen, 112, 107).

For the preparation of luteolin in quantity, Perkin (Chem. Soc. Trans., 1896, 69, 206, 799) employs weld extract.

300 gms. of the extract dissolved in 3 litres of water is treated with 100 c.c. of hydrochloric acid (33 per cent.), and the mixture is digested at the boiling temperature for some hours. A quantity of a black resinous substance separates, which is collected while hot, and the filtrate, which contains the colouring matter, is allowed to stand for twelve hours. A brown precipitate of impure luteolin is slowly deposited, and is collected, washed, and dissolved in a little hot alcohol. On pouring this solution into ether, the main bulk of the impurity is precipitated, and the ethereal liquid on evaporation yields a yellow residue, which is crystallised from dilute alcohol. The product in addition to luteolin contains apigenin (Chem. Soc. Trans., 1900, 77, 1315), and the latter can only be removed with certainty by the following method:—

The mixture dissolved in boiling glacial acetic acid is treated with a few drops of strong hydrochloric acid; this causes the almost immediate separation of luteolin as hydrochloride, whereas the apigenin remains in solution. The hydrochloride is collected, decomposed by water, and the luteolin crystallised from dilute alcohol.

Luteolin, $C_{15}H_{10}O_6$, crystallises in yellow needles or leaflets, melting-point 327—329° (Perkin), 327° (v. Kostanecki, Rozycki, and Tambor, Ber., 1900, 33, 3410), soluble in alkaline solutions with a yellow coloration. With alcoholic lead acetate it gives a bright yellow precipitate and with alcoholic ferric chloride a green solution.

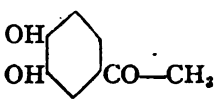
Luteolin sulphate, $C_{15}H_{10}O_6 . H_2SO_4$, orange-red needles; *luteolin hydriodide*, $C_{15}H_{10}O_6 . HI$, orange prisms; *luteolin hydrobromide*, $C_{15}H_{10}O_6 . HBr, H_2O$, ochre needles; and *luteolin hydrochloride*, $C_{15}H_{10}O_6 . HCl, H_2O$ (Perkin, *loc. cit.*), are readily prepared by the action of the acids on luteolin in the presence of boiling acetic acid. By treatment with water these compounds are quantitatively decomposed into luteolin and acid.

Monopotassium luteolin, $C_{15}H_9O_6K$, fine yellow needles, from luteolin by means of alcoholic potassium acetate, is decomposed by boiling water with separation of luteolin. The *sodium* compound, $C_{30}H_{19}O_{12}Na$, behaves similarly.

Tetra-acetyl luteolin, $C_{15}H_6O_6(C_2H_3O)_4$, Perkin (also Herzig, Ber., 1896, 29, 1013), colourless needles, melts at 221—223° (Perkin), 225—227° (Herzig). *Tetrabenzoyl-luteolin*, $C_{15}H_6O_6(C_7H_5O)_4$, colourless needles, melts at 200—201° (Perkin).

Dibromluteolin, $C_{15}H_8Br_2O_6$, yellow needles, melts at 305°.

By the action of nitric acid on luteolin Rochleder (Zeitsch. für Chem., 1886, 602) obtained oxalic acid, and with fused alkali *protocatechuic acid* and *phloroglucinol*. Digested with boiling 50 per cent. potassium hydroxide solution, phloroglucinol and *acetyl catechol* are produced (Perkin and Horsfall, Chem. Soc. Trans., 1900, 77, 1322)—



When methylated with methyl iodide luteolin yields, in addition to luteolin trimethyl ether, also methyl-luteolin trimethyl ether (Perkin and Horsfall).

Luteolin trimethyl ether, $C_{15}H_7O_3(OCH_3)_3$, lemon-yellow needles, melting-point 161—163°, forms a *monoacetyl* derivative,

$$C_{15}H_6O_3(C_2H_3O)(OCH_3)_3,$$

colourless prisms, melting-point 156—158°, and with alcoholic potash gives a bright yellow crystalline salt, which is decomposed by water.

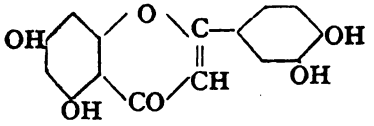
On hydrolysis with alcoholic potash at 170° the trimethyl ether gives *veratric acid*, and *phloroglucinol monomethyl ether*, which was isolated in the form of disazobenzene-phloroglucinol monomethyl ether, orange needles, melting-point 251—252°.

Methyl-luteolin trimethyl ether, $C_{16}H_9O_3(OCH_3)_3$, melts at 191—192°, and the *monoacetyl* derivative, $C_{16}H_8O_3(OCH_3)_3(C_2H_3O)$, at 175—176°. By means of alcoholic potash *veratric acid* and *methyl phloroglucinol methyl ether* (identified as disazobenzene methyl phloro-

glucinol monomethyl ether, orange-red needles, melting-point 198—201°) are produced.

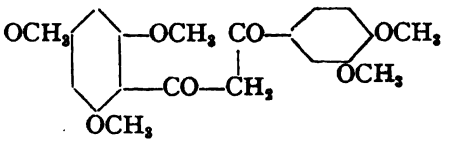
By digestion with boiling hydriodic acid *methyl-luteolin*, $C_{16}H_{12}O_6$, yellow leaflets, is formed, melting-point about 307—309°, which gives an acetyl compound melting at 235—236°.

Perkin (*loc. cit.*) assigned to luteolin the constitution of a tetrahydroxyflavone—



and the more recent synthesis of this colouring matter by v. Kostanecki, Rozycki, and Tambor (*loc. cit.*) has indicated that this formula is correct.

When *phloracetophenone trimethyl ether* is condensed with *ethyl veratrate* it gives 2 : 4 : 6 : 3′ : 4′ *pentamethoxybenzoyl acetophenone*—



and this by long digestion with boiling hydriodic acid (sp. gr. 1·96) is converted into luteolin.

Though luteolin when digested with alcoholic potash and ethyl iodide in the ordinary manner gives only a triethyl ether, owing to the presence of an hydroxyl in the ortho position to the carbonyl group, when an excess of the reagents is employed, luteolin tetraethyl ether, $C_{15}H_6O_2(OEt)_4$, colourless needles, melting-point 153—155°, can readily be obtained (Perkin, Chem. Soc. Proc., 1912, 28, 328). Though quercetin pentamethyl ether on nitration readily gives the 6′ mononitro derivative (Watson, Chem. Soc. Trans., 1914, 105, 338), luteolin tetraethyl ether yields in similar circumstances only the *tetranitro* compound, $C_{15}H_2O_2(NO_2)_4(OEt)_4$, colourless prisms, melting-point 196°. On the other hand, the introduction of only one nitro group can be effected by nitrating mono-brom-luteolin tetraethyl ether (see below) (Perkin and Watson, *ibid.*, 1915, 107, 199). Bromine (4 molecules) in acetic acid yields *bromluteolin tetra-ethyl ether perbromide*, $C_{15}H_5O_2(OEt)_4Br$, HBr_3, orange-yellow prisms, melting-point 161° (decomp.), and this on boiling with water gives *bromluteolin tetraethyl ether* and *tetrabromluteolin tetraethyl ether*.

With bromine (1 molecule) in acetic acid solution, *bromluteolin*

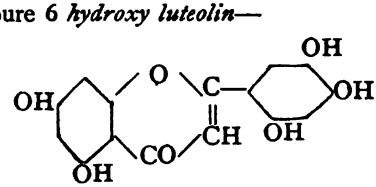
tetraethyl ether hydrobromide, $C_{15}H_5O_2(OEt)_4Br$, $HBrC_2H_4O_2$, pale yellow hair-like needles, is obtained, which when boiled with water gives *bromluteolin tetraethyl ether*, $C_{15}H_5O_2Br(OEt)_4$, colourless hexagonal plates, melting-point 183°, whereas by brominating luteolin tetraethyl ether with 2 molecules of the halogen in acetic acid solution in presence of sodium acetate, *tetrabromluteolin tetraethyl ether*, colourless crystals, melting-point 111—114°, is formed.

Brom-6' nitroluteolin tetraethyl ether, $NO_2C_{15}H_4O_2Br(OEt)_4$, pale yellow rhombs, melting-point 170—171°, on reduction in alcoholic solution with stannous chloride and hydrochloric acid, gives *brom-6' amino-luteolin tetraethyl ether*, $C_{15}H_4O_2Br(OEt)_4NH_2$, yellow prisms, melting-point 165—169°. This forms the *hydrochloride*

$$C_{15}H_4O_2Br(OEt)_4NH_2HCl\ H_2O,$$

bright yellow needles, which when dried over soda lime become scarlet and melt at 187° (decomp.); with *stannic chloride* it forms the salt $(C_{22}H_{26}O_6NBr)_4H_4SnCl_6$, crimson prisms. By means of sodium nitrite the amino hydrochloride yields in the usual way, crystalline *bromluteolin tetraethyl ether diazonium hydrochloride*, and from this by boiling with water *brom-6 hydroxy-luteolin tetraethyl ether*, $C_{15}H_4O_2Br(OEt)_4OH$, yellow needles, melting-point 255°, the *acetyl derivative* of which crystallises in white needles, melting-point 270—272°, is produced.

This latter, probably owing to its insolubility, is not readily attacked by hydriodic acid (D1·7), the first product of the reaction being apparently *brom-6-hydroxy-luteolin diethyl ether*, $C_{15}H_4O_2Br(OH)_2(OEt)_2$, the *acetyl* compound of which melts at 213°. The more drastic action of the hydriodic acid, employing also acetic anhydride, gave a small quantity of a compound crystallising in yellow needles, soluble in alkaline solutions with a yellowish-brown colour, and which was probably an impure 6 *hydroxy luteolin*—



The acetyl compound melted at 250—256°.

When air is aspirated through alkaline solutions of luteolin (and also those of chrysin and apigenin), oxidation does not occur. This property, according to Perkin (*loc. cit.*) distinguishes the colouring matters of the flavone from those of the flavonol class, which are readily oxidised by this treatment.

It has already been stated that weld contains a second colouring matter, Apigenin (*v.* Parsley).

Dyeing Properties of Weld.—The importance of weld as a dyestuff in silk and wool dyeing has greatly diminished in consequence of its low colouring power compared with quercitron bark, flavin, and old fustic. This in one respect is unfortunate, because, of all the natural yellow colouring matters, it yields the purest and fastest shades. In conjunction with aluminium and tin mordants it gives very bright pure lemon-yellow colours, and these do not change to an olive or reddish tint as in the case with other vegetable yellows. With chromium and iron mordants weld gives yellowish and greenish olives respectively. For yellow, wool and silk are mordanted with alum and tartar in the usual manner and dyed subsequently in a decoction of weld with the addition of chalk to the dye-bath. Weld alumina yellow is to some extent still employed in this country for certain army cloths and braid. For silk dyeing, weld extract is manufactured in small quantity, and is used for the production of yellow and olive colours.

Dyer's Broom.

Genista tinctoria, Linn. (*Dyer's broom, Dyer's greenweed; Genet, Genestrole, Trentanel*, Fr.; *Ginster*, Ger.) is found in the pastures, thickets, and waste places throughout Central and Southern Europe, across Russian Asia to the Baikal, and northward to Southern Sweden. It is frequent in the greater part of England, but rare in Ireland and Scotland. The fact that it contains a yellow colouring matter is recorded by numerous writers, and the following embody the principal references to the dyeing and general properties of the plant: Bancroft ("Philosophy of Permanent Colours," 1813, 2, 108); Gmelin ("Handbook of Chemistry," 16, 517); Berthollet ("On Dyeing," 1824, 2, 242); Gonfreville ("L'Art de la Teinture des Laines," 501); Leuchs ("Farben u. Farbekunde," 1846, 2, 309), and Schützenberger ("Traité des Matières Colorantes," 1867, 4, 422).

To isolate the colouring matters, a hot aqueous extract of the plant is treated with lead acetate solution, and the pale yellow viscous precipitate is collected and decomposed by means of boiling dilute sulphuric acid. The clear liquid decanted from the lead sulphate deposits on cooling a dull yellow powder; this is filtered off, dissolved in a little alcohol, and the solution poured into a large volume of ether, causing the separation of a dark-coloured resinous impurity. The clear liquid is evaporated, yielding a yellow crystalline residue, which consists of two substances. To separate these, advantage is taken of the fact that, with sulphuric acid in the presence

of acetic acid, one only of these compounds gives an insoluble sulphate. This is collected and decomposed with water and the product crystallised from dilute alcohol. It is obtained as yellow needles, and was found to be identical with the *luteolin* of weld (*Reseda luteola*) (Perkin and Newbury, Chem. Soc. Trans., 1899, 75, 830).

Genistein, $C_{14}H_{10}O_5$, the second colouring matter of dyer's broom, is present in the mother liquors obtained during the purification of the luteolin, and also in considerable quantity in the filtrate from the lead precipitate, from which it is most readily isolated. To the boiling liquid ammonia is added, causing the separation of a lemon-yellow precipitate, which is collected and decomposed with boiling dilute sulphuric acid. The clear liquid is extracted with ether, and the extract evaporated, leaving a brownish crystalline mass. It is purified by crystallisation from acetic acid, and by conversion into the acetyl derivative.

Genistein crystallises in long colourless needles; melting-point 291—293° (Perkin and Horsfall, Chem. Soc. Trans., 1900, 77, 1312); soluble in alkalis with a pale yellow coloration. Alcoholic ferric chloride gives a dull-red violet coloration, and alcoholic basic lead acetate a lemon-yellow precipitate.

Triacetylgenistein, $C_{14}H_7O_5(C_2H_3O)_3$, colourless needles, melting-point, 197—201°; and *tetrabromgenistein*, $C_{14}H_6Br_4O_5$, colourless needles, melting-point above 290°, have been described.

On digestion with boiling 50 per cent. potassium hydroxide, genistein gives *phloroglucinol* and *p-hydroxyphenylacetic acid.*

By methylation with methyl iodide in the usual manner, genistein dimethyl ether and methylgenistein dimethyl ether are produced.

Genistein dimethyl ether, $C_{14}H_8O_3(OCH_3)_2$, forms colourless leaflets, melts at 137—139°, and gives the *monacetyl* compound,

$$C_{14}H_7O_3(C_2H_3O)(OCH_3)_2,$$

minute colourless needles, melting-point 202—204°. When decomposed with alcoholic potash, it forms *methoxyphenylacetic acid* and *phloroglucinol-monomethyl ether* (identified by means of its disazobenzene derivative).

Methylgenistein dimethyl ether,

$$CH_3 . C_{14}H_7O_3(OCH_3)_2,$$

melts at 202°; and the *acetyl* derivative,

$$CH_3 . C_{14}H_6O_3(C_2H_3O)(OCH_3)_2,$$

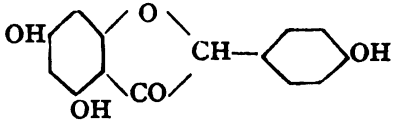
forms colourless needles, melting-point 212—214°. With alcoholic potash it gives *methoxyphenylacetic acid* and probably *methylphloroglucinol-monomethyl ether.*

Genistein diethyl ether, $C_{14}H_8O_3(OC_2H_5)_2$, forms colourless needles, melting-point 132—134°; whereas *acetylgenistein diethyl ether*,

$$C_{14}H_7O_3(C_2H_3O)(OC_2H_5)_2,$$

melts at 168—170°. Alcoholic potash gives *p-ethoxyphenylacetic acid*.

According to Perkin and Horsfall, genistein is most probably a *trihydroxyphenylketocumaran*—



Genistein is a feeble colouring matter, and upon woollen cloth gives, with chromium mordant, a pale greenish-yellow; with aluminium mordant, a very pale yellow; and with iron mordant, a chocolate-brown shade.

Dyeing Properties of Dyer's Broom.—In this respect there is a close resemblance between dyer's broom and weld. The dyeing power of the former is distinctly the weaker of the two; otherwise the only point of difference worthy of mention is that shown by the iron mordant, which, in the case of dyer's broom, gives a duller and more drab-coloured shade. Luteolin is also present in the *Digitalis purpurea* (digito-flavone), (Fleischer and Fromm, Ber., 1899, 32, 1184; v. Kostanecki and Diller, *ibid.*, 1901, 34, 3577), and in the flowers of *Antirrhinum majus* (Wheldale and Bassett, Biochem. Jour., *loc. cit.*).

Fukugi.

The Japanese dyestuff "fukugi" (botanical origin unknown) has, at least until recently, been employed to a considerable extent in Japan as a mordant dyestuff. It consists of the wood of a tree which when ground forms an almost colourless powder, the extract of which is sold in the form of brittle rectangular cakes of a yellowish-brown colour.

Fukugetin, $C_{17}H_{12}O_6$, the colouring matter, forms minute canary-yellow prismatic needles melting at 288—290° (Perkin and Phipps, Chem. Soc. Trans., 1904, 85, 58). It dissolves in alkaline solutions with a yellow colour, and gives with alcoholic lead acetate an orange-yellow precipitate and with alcoholic ferric chloride a brown-black coloration.

Crystalline acetyl and benzoyl derivatives of this colouring matter could not be obtained, but the *bromine* compound, $C_{17}H_{10}O_6Br_2$, minute flat needles, melting-point 280°, is readily prepared by the action of bromine on fukugetin in the presence of acetic acid.

Fukugetin dyes mordanted fabrics shades which are almost identical with those given by luteolin—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Dull orange-yellow,	Orange-yellow,	Bright yellow,	Olive brown,

and resembles this colouring matter in that its alkaline solution is not oxidised on exposure to air. By fusion with alkali fukugetin gives *phloroglucinol* and *protocatechuic acid.*

The dyeing properties of "fukugi" are analogous to those of weld. The similarity in shade indeed is so marked that except in point of strength—for fukugi is a stronger dye than weld—it is impossible to distinguish between them.

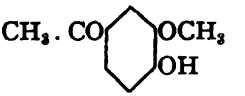
SCOPARIN.

Scoparin, the colouring matter of the *Cytisus scoparius* (Link.), has been investigated by Stenhouse (Annalen, 78, 15), by Hlasiwetz (Annalen, 138, 190), and by Goldschmiedt and Hemmelmayer (Monatsh., 14, 202).

Scoparin, $C_{20}H_{20}O_{10}$, $5H_2O$?, crystallises in small yellow needles, melting-point 202—219°, and is soluble in alkaline liquids with a pale yellow colour. From a hot aqueous solution it is deposited on cooling in a gelatinous condition. The following derivatives have been prepared:—

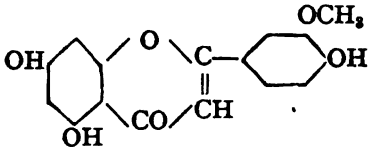
Hexa-acetylscoparin, $C_{20}H_{14}O_{10}(COCH_3)_6$, colourless prisms, melting-point 255—256°; *hexabenzoyl scoparin*, $C_{20}H_{14}O_{10}(C_7H_5O)_6$, yellow crystalline powder, melting-point 148—150°; *scoparin ethyl ether*, $C_{20}H_{19}O_9(OC_2H_5)$, needles, melting-point 272°; and *acetylscoparin ethyl ether*, $C_{20}H_{14}O_9(OC_2H_5)(C_2H_3O)_5$, needles, melting-point 140—141° (Goldschmiedt and Hemmelmayer).

By fusion with potash scoparin gives *vanillic acid*, *protocatechuic acid*, *acetic acid*, and *phloroglucinol* (H.), and by the more gentle action of the alkali *phloroglucinol* and *acetylcatechol monomethyl ether*—



(Goldschmiedt and Hemmelmayer; Perkin, Chem. Soc. Proc., 1899, 15, 123). With boiling hydriodic acid scoparin yields 1 molecule of methyl iodide, and a new colouring matter *scoparein* (Perkin), which dyes shades almost identical with those given by luteolin. Scoparin itself is but a feeble dyestuff, and its tinctorial properties are almost indistinguishable from those of vitexin (*Vitex*

littoralis, A. Cunn.). According to Perkin (Chem. Soc. Trans., 1900, 77, 423), scoparin is probably *methoxyvitexin*, and whereas vitexin is closely related to apigenin, scoparin is derived from *luteolin methyl ether*—



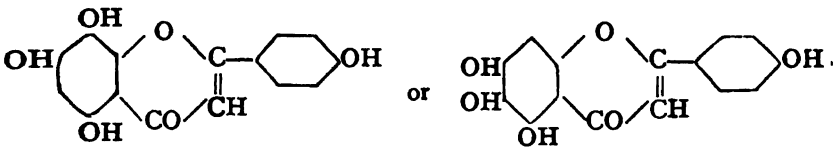
SCUTELLARIA ALTISSIMA.

Scutellarin.—If the flowers and leaves of *Scutellaria altissima* are extracted with water the solution on keeping deposits crystals of *scutellarin*, $C_{21}H_{18}O_{12}$ (Molisch and Goldschmiedt, Monatsh., 1901, 22, 68; Goldschmiedt and Zerner, *ibid.*, 1910, 31, 439). It melts above 310°, is sparingly soluble in the usual solvents, and the alcoholic solution gives with lead acetate a red precipitate, and with ferric chloride a green coloration passing into red on heating. With the haloid acids and sulphuric acid in the presence of acetic acid orange-red crystalline oxonium compounds separate, which are readily decomposed in contact with water. *Penta-acetylscutellarin*, $C_{21}H_{13}O_{12}(C_2H_3O)_5$, is colourless, melts at 263—265°, and from this by gentle hydrolysis scutellarin can be regenerated. On fusion with alkali *p-hydroxybenzoic acid* and a second substance crystallising in leaflets are produced. When concentrated sulphuric acid is added to scutellarin suspended in water until a clear liquid is obtained, on dilution *scutellarein*, $C_{15}H_{10}O_6$, is precipitated and *glycuronic acid* is present in the solution. The hydrolysis of scutellarin cannot be effected by means of dilute acids, though this takes place, however, when its suspension in glacial acetic acid is treated with sulphuric acid, the oxonium sulphate thus obtained being evidently that of scutellarein.

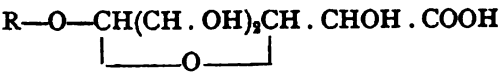
Scutellarein when pure forms yellow crystals melting above 300° and is soluble in alkaline solutions with a yellow colour. Lead acetate solution gives a reddish-yellow precipitate and ferric chloride a reddish-brown coloration. On acetylation scutellarein gives the colourless *tetra-acetyl* compound, $C_{15}H_6O_6(OAc)_4$, melting-point 235—237°, whereas with ethereal diazomethane *scutellarein trimethyl ether*, $C_{15}H_7O_3(OMe)_3$, melting-point 189—190°, is formed. By means of methyl alcoholic potash and methyl iodide the *tetramethyl* compound, $C_{15}H_6O_3(OMe)_4$, can be obtained in small amount. By fusion with potassium hydrate *p-hydroxybenzoic* acid and *phloroglucinol* (?) are produced, whereas a boiling 12 per cent. solution

of the alkali gives *p-hydroxyacetophenone* and a substance which gives the pine-wood reaction of phloroglucinol. Dilute nitric acid gives picric, oxalic, and 3·5 *dinitro*-4 hydroxybenzoic acids.

Scutellarein, according to Goldschmiedt and Zerner, is a 1 : 3 : 4 : 4′ or 1 : 2 : 3 : 4′ tetrahydroxyflavone—



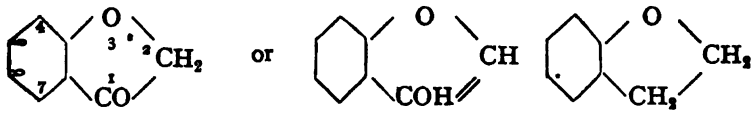
Scutellarin can probably be represented as



R in this formula representing the scutellarein nucleus.

Coumaranone Group.

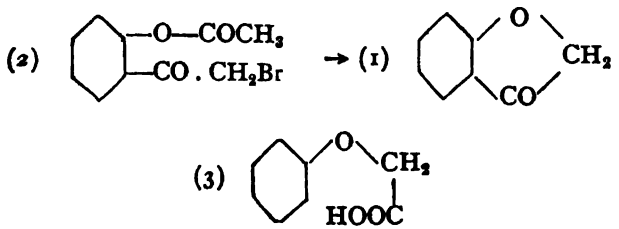
Though colouring matters derived from coumaranone (keto-cumaran) have not as yet been isolated from natural sources, there



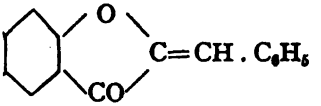
Ketocumaran. Cumaran.

is some probability of their presence in certain flowers, and they are not only historically connected with the earlier attempts to synthesise the flavones, but have in certain instances been successfully converted into flavonols.

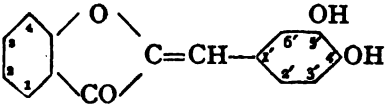
Coumaranone (1) is obtained (Friedländer and Neudörfer, Ber., 1897, 30, 1077) by boiling acetyl *o*-hydroxy acetophenone bromide (2) with an aqueous suspension of chalk, or by the action of dehydrating agents on phenoxyacetic acid (3)—



(Friedländer, Ber., 1899, 32, 1867), and consists of colourless needles, melting-point 97°. It condenses with aldehydes in the presence of hydrochloric acid with formation of benzylidenecoumaranone—

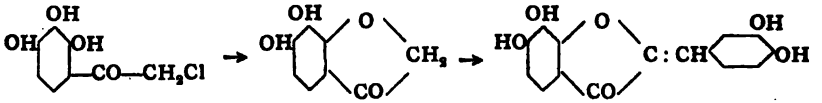


which was at first considered by Friedländer and Neudörfer (Ber., 1897, 30, 1077) to consist of flavone. On substituting protocatechuic aldehyde for benzaldehyde these authors obtained the dihydroxy compound—

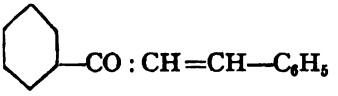


and this is a strong dyestuff which gives on aluminium mordanted fabrics an orange, and with iron and chromium mordants brown coloured shades.

The first colouring matter of this group was, however, prepared in 1896 by Friedländer and Rüdt (Ber., 29, 878) from chlorogallacetophenone and benzaldehyde—



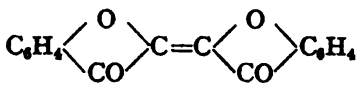
and from the analogous resacetophenone derivative other hydroxy compounds of this group were obtained later. These are of an orange or orange-red colour, as a rule form oxonium salts, and those possessing tinctorial property dye alum mordant a much more orange shade than the flavone colouring matters. There is indeed a close resemblance in this latter respect between these compounds and the colouring matters derived from chalkone—



(Perkin, Chem. Soc. Trans., 1904, 85, 1465), for butein (see below) and the 3 : 4 : 3′ : 4′ tetrahydroxybenzylidene coumaranone of Friedländer and Rüdt give almost identical shades. The benzylidene coumaranones dissolve in sulphuric acid with the production of a red or red-violet coloration, and can thus again be distinguished from flavones which in this manner give either colourless or pale yellow solutions.

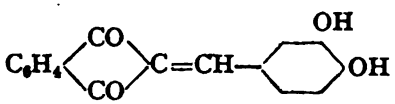
In 1896 Kesselkaul and v. Kostanecki (Ber., 29, 1886) suggested that judging by its colour reactions the colouring matters of Friedländer and Rüdt were not, as these authors suggested, flavone but rather coumaranone derivatives, and the true constitution of these substances became evident on the synthesis of flavone itself by Feuerstein and v. Kostanecki (*loc. cit.*). That benzylidenecoumaranones can be converted into flavanol derivatives has been shown by Auwers and Müller (Ber., 1908, 41, 4203), and this transformation is discussed in a later chapter.

Coumaranone is also interesting as the source of ox-indigo—



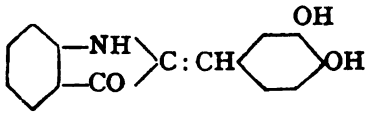
the oxygen analogue of indigotin. This crystallises in yellow prisms, but does not possess any tinctorial value.

Analogous colouring matters can be obtained from diketohydrindene (indandione), this also possessing the reactive methylene group, with aldehydes. Thus by heating this compound with protocatechuic aldehyde at 110—120° v. Kostanecki prepared the dihydroxybenzylidene derivative—



which consists of brownish-yellow needles, melting-point 257°, soluble in alkaline solutions with a red-violet colour and gives yellow shades on aluminium mordanted fabrics.

From indoxyl also in a similar way Perkin and Thomas (Chem. Soc. Trans., 1909, 95, 798) prepared dihydroxybenzaldehydeindogenide—



crystallising in orange-red needles, and producing with aluminium mordanted fabrics dull scarlet shades.

CHAPTER VI.

THE CHALKONE AND FLAVANONE GROUPS.

Butea frondosa.

Chalkone or benzylideneacetophenone and its hydroxy derivatives have been already referred to in connection with the synthesis of flavone compounds. Chalkone itself is readily prepared by the interaction of acetophenone and benzaldehyde (Claisen, Ber., 20, 257)—

$$C_6H_5 . CO . CH_3 + C_6H_5COH \rightarrow C_6H_5 . CO . CH_2 . CHOH . C_6H_5 \rightarrow C_6H_5 . CO . CH : CH . C_6H_5 + H_2O$$

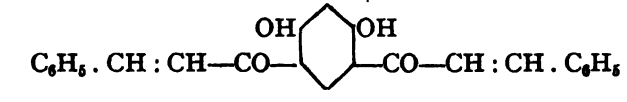
It consists of yellow rhombic prisms, melting-point 57—58°.

When submitted to hydrolysis it is reconverted into the aldehyde and ketone, a reaction which is the reversal of that given above—

$$C_6H_5 . CO . CH : CH . C_6H_5 \rightarrow C_6H_5 . CO . CH_2 . CH . OH . C_6H_5 \rightarrow C_6H_5 . CO . CH_3 + C_6H_5CH(OH)_2 \rightarrow C_6H_5 . COH + H_2O$$

By the employment of hydroxyacetophenones and hydroxybenzaldehydes, in general previously methylated, numerous chalkone derivatives have been obtained by v. Kostanecki and his co-workers. But one natural colouring matter of this group known as butein has at present been isolated, and the synthetically prepared compounds have been more specially interesting owing to their employment for the synthesis of the flavonol group of colouring matters.

Ryan and O'Neill (*loc. cit.*) by the aid of diacetoresorcinol have obtained dichalkone compounds. Thus diacetoresorcinol dimethyl ether and benzaldehyde form dibenzylidendiacetoresorcinol dimethyl ether, and this by the action of aluminium chloride is dimethylated with production of the free hydroxy compound—

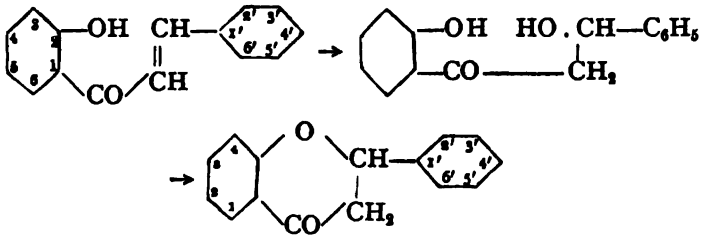


It was obtained as yellow crystals melting at 196—198°.

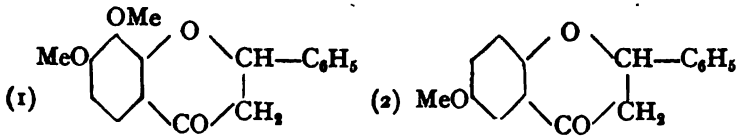
Interesting is the fact shown by these authors (*ibid.*, 1915, 8, 167) that by a variation in its method of preparation four distinct varieties of this dichalkone can be produced.

Whereas three of these designated as α, β and δ are stereo-isomers, the fourth or γ variety is structurally related to the other three.

When 2-hydroxychalkone is digested at the boiling temperature with alcoholic sulphuric acid, ***flavanone*** (dihydroflavone) is produced according to the following scheme:—



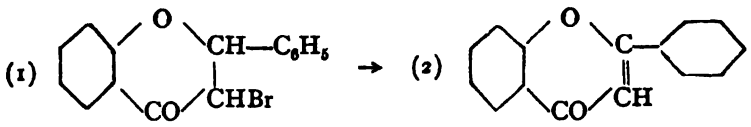
and this is the method generally adopted for the synthesis of flavanone derivatives. On the other hand, though as a rule a chalkone only is produced by the interaction of aldehyde and hydroxyketone, when gallacetophenone dimethyl ether (Woker, v. Kostanecki, and Tambor, Ber., 1903, 36, 4235) or quinacetophenone monomethyl ether (v. Kostanecki and Lampe, *ibid.*, 1904, 37, 773) are condensed with benzaldehyde in the presence of sodium hydroxide the respective flavanones (1 and 2) are thus directly obtained—



On hydrolysis the flavanones yield chalkones, a reversal of the equation given above. In the case of butin and its derivatives which are described later, this not only takes place in presence of alkali, but also on digestion with alcoholic sulphuric acid. The reaction in these cases is not unidirectional, and the conversion of flavanone into chalkone, or chalkone into flavanone, is never complete.

Chalkones which contain hydroxyls in the ortho position to one another, in the position 3′ : 4′ are powerful colouring matters, whereas flavanones possessing similar hydroxyls are not dyestuffs, as indeed their constitution indicates. During the dyeing operation, employing mordanted woollen material hydrolysis occurs (compare butin), and the shades produced by them are in reality those derived from the chalkone. Flavanone crystallises in small colourless needles, melting at 75—76°.

As already pointed out, the bromflavanone (1) by elimination of hydrobromic acid readily yields flavone (2)—



and, again, flavanones may be converted into flavonols, a reaction which is described later on.

Butea frondosa.

The *Butea frondosa*, also called *Dhak* or *Pulas*, is a fine tree, 30—40 feet high, belonging to the order *Leguminosæ*. It is common throughout India and Burma, and is found in the North-West Himalaya, as far as the Jhelum River. The flowers, which in the dried condition are known as tísu, késú, kesuda or palás-képpúl, have a bright orange colour, and, although they are much larger, closely resemble in appearance the common gorseflower (*Ulex europæus*), with which, indeed, they are botanically allied. Large quantities of the flowers are collected in March and April, and employed by the natives to produce a yellow dye, much used during the "Holi" festival. The dyeing operation, which consists in steeping the material in a hot or cold decoction of the flowers, is virtually a process of staining, because the colour can be readily washed out. On the other hand, a more permanent result is sometimes produced either by first preparing the cloth with alum and wood ash or by adding these substances to the dye-bath.

From the *Butea frondosa* is also obtained the so-called "Butea gum" or "Bengal kino," employed by the natives for tanning leather, and the tree is of additional interest because in many parts of India the lac insect (*Coccus lacca*) is reared upon it. This latter, as is well known, causes the formation of stick lac, from which shellac and lac dye are prepared.

Butin, $C_{15}H_{12}O_5$.—The flowers are extracted with water, and the extract digested boiling with a little sulphuric acid. A light viscous precipitate devoid of dyeing property separates, and this is removed while hot and the filtrate left over-night. The clear liquid is now decanted from a small quantity of tarry substance, and partially evaporated on the water-bath. A further quantity of a black viscous precipitate thus separates, and when this has been removed the filtrate, after some days, deposits crystals of the colouring principle. For purification the product is dissolved in a little alcohol, the mixture poured into ether, and the solution well washed with water. The liquid is evaporated, and the residue repeatedly crystallised from dilute alcohol (Perkin and Hummel, Chem. Soc. Trans., 1904, 85, 1459).

Butin crystallises from alcohol in colourless needles with $\frac{1}{2}H_2O$, melting-point 224—226°, and from water in pale yellow needles with $2H_2O$; dissolves in alkaline solutions with a pale orange-red tint, and gives with alcoholic acetate of lead a faintly yellow almost colourless precipitate. It forms a *triacetyl* derivative, $C_{15}H_9O_5(C_2H_3O)_3$, colourless leaflets, melting-point 123—125°, and a *tribenzoyl* compound, $C_{15}H_9O_5(C_7H_5O)_3$, colourless needles, melting-point 155—157°. On fusion with alkali at 200—220° butin gives *protocatechuic acid* and *resorcinol*.

When butin is boiled with dilute potassium hydroxide solution, the pale-coloured liquid becomes much darker, and on acidifying an orange crystalline precipitate separates which consists of *butein*.

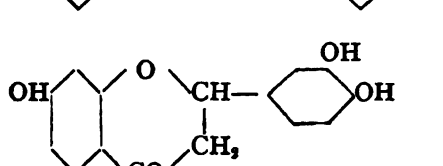
Butein, $C_{15}H_{12}O_5$, H_2O, needles, melts at 213—215°; dissolves in alkaline solutions with a deep orange-red colour, and with alcoholic lead acetate gives a deep-red precipitate. *Acetylbutein*, $C_{15}H_8O_5(C_2H_3O)_4$, pale-yellow needles, melts at 129—131°.

When fused with alkalis butein gives *resorcinol* and *protocatechuic* acid, whereas by the action of boiling 50 per cent. potassium hydroxide solution, *protocatechuic* acid and *resacetophenone* are produced.

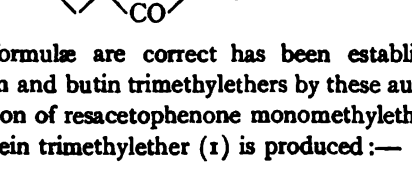
By methylation with methyl iodide butin gives *butin trimethylether*, $C_{15}H_9O_2(OCH_3)_3$, colourless plates, melting-point 119—121°, and also *butein trimethylether*, $C_{15}H_9O_3(OCH_3)_3$, yellow leaflets, melting-point 156—158°. In a similar manner, butein yields not only butein trimethylether, but also butin trimethylether.

The constitution assigned to butein by Perkin and Hummel is that of a *tetrahydroxybenzylidene acetophenone* (*tetrahydroxychalkone*) (1), and to butin that of the corresponding *flavanone* (2):—

(1)

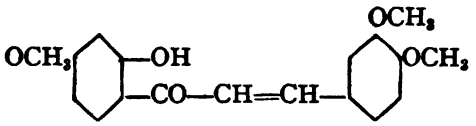


(2)



and that these formulæ are correct has been established by the synthesis of butein and butin trimethylethers by these authors. Thus by the condensation of resacetophenone monomethylether with veratric aldehyde, butein trimethylether (1) is produced:—

(1)



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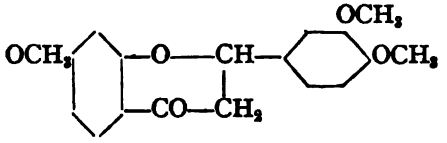
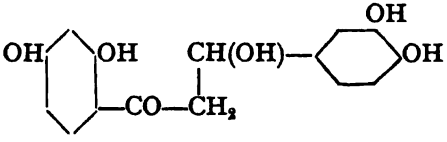


and this, when digested with boiling dilute alcoholic sulphuric acid, a method devised by v. Kostanecki and his colleagues (Ber., 1904, 37, 784, 773, 779), gives butin trimethylether (2).

Somewhat later (Ber., 1911, 44, 3502) Göschker and Tambor prepared butein itself by treating protocatechuic aldehyde and resacetophenone in boiling alcohol with potassium hydroxide solution and found this to be identical in all respects with the natural product. *Butein methylether*, yellow needles, melting-point 185°, 3′ : 4′ *butein dimethylether*, yellow prisms, melting-point 203°, and *butein tetramethylether* (Ber., 1912, 45, 186), colourless needles, melting-point 89°, were also described.

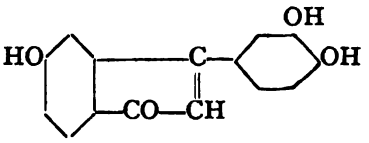
Butein itself is also converted into butin by means of dilute alcoholic sulphuric acid, and the butin can again be transformed into butein by the action of potassium hydroxide solution. With alcoholic potash butin trimethylether also gives butein trimethylether, and these changes are readily explained if it is assumed that the intermediate compound or its trimethyl ether—



is the first product of the reaction in each case, and that this subsequently, by loss of water, passes into either chalkone or flavanone, or both.

When butein dissolved in acetic acid is treated with a few drops of sulphuric acid, and the solution is boiled, a new substance gradually separates in the form of crystals, which possess a beetle-green iridescence, and dissolves in alkaline solutions with a deep-blue colour. The acid liquid decanted from the crystals, on dilution with water, gives a brown precipitate soluble in alkalis with a bluish-violet coloration, which dyes mordanted calico shades of a similar character to those yielded by anthragallol. It appears probable that

this more soluble substance represents the first product of the reaction, and is subsequently converted into the green iridescent compound. A consideration of the formula of butein renders it unlikely that these new substances are anthraquinone derivatives; on the other hand, it is suspected that by loss of water ring formation takes place, and that an indone derivative of the following type is first produced :—



Butin and butein dye mordanted woollen cloth identical shades, though as butin gives with an alcoholic lead acetate a practically colourless precipitate, it is not to be regarded as a colouring matter. In other words, butin is merely a colouring principle, and is converted during the dyeing operation by the action of the mordant into the colouring matter butein.*

The following shades are obtained :—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Reddish-brown,	Brick-red,	Full-yellow,	Brownish-black,

and these are strikingly similar to those yielded by some of the hydroxybenzylidenecoumaranones artificially prepared by Friedländer and Rüdt (Ber., 1896, 29, 879) (see above).

The butea flowers contain but a trace of free butin or butein, and the glucoside present, which has not yet been isolated, is probably that of butin. This glucoside does not decompose readily during the dyeing process, hence the flowers do not dye mordanted cotton. In wool-dyeing, where acid-baths are employed, a better result is obtained, although in this case the shades possess but little strength. If the glucoside is first hydrolysed by boiling the flowers with dilute hydrochloric acid, or if sulphuric acid is employed, and the acid then neutralised with sodium carbonate, on evaporation a material is obtained which readily dyes by the usual methods. Such products give the following shades: with chromium, deep terra-cotta; with aluminium, a bright orange; with tin, bright yellow; and with iron, a brownish-olive. The chromium colour is characteristic, and is much redder in tint than that yielded by any known natural yellow dye.

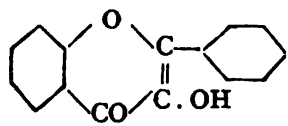
* This result has been criticised by Göschker and Tambor, who by the employment of mordanted calico obtained from butin very weak shades. It is, however, certain that by the use of mordanted wool a conversion of butin into butein occurs.

CHAPTER VII.

FLAVONOL GROUP.

Introduction — Flavonol—Galanga Root — *Delphinium consolida* Flowers — *Robinia pseudacacia* Flowers — Young Fustic—Yellow Cedar—Quercitron Bark—*Thuya occidentalis*—*Sophora japonica*—Onion Skins—Heather—*Thespasia macrophylla*—*Eucalyptus macrorhyncha*—*Podophyllum emodi*—Clover Flowers—*Prunus emarginata*—Persian Berries—*Rhamnus catharticus*—Asbarg—Yellow Wallflower—Old Fustic—Osage Orange—Jak-wood—*Myrica nagi*—Cotton Flowers—African Marigold.

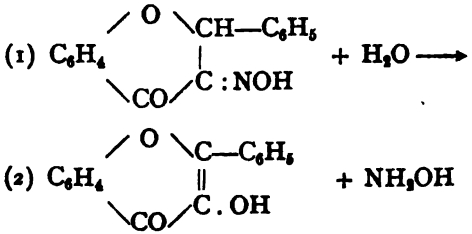
FLAVONOL.



IT is usual to subdivide the great family of yellow colours derived from flavone into two classes, *flavone* and *flavonol*, and the latter group is distinguished by the fact that the hydrogen in the γ-pyrone ring of these compounds is substituted by hydroxyl, whereas in the former it is not.

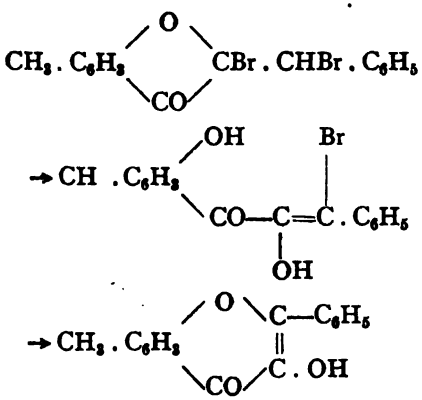
Flavonol, so designated by v. Kostanecki, was synthesised by v. Kostanecki and Szabránski (Ber., 1904, 37, 2819) in the following manner:—

By the action of amyl nitrite and hydrochloric acid in alcoholic solution on flavanone, isonitrosoflavanone (1), melting-point 158—159°, is produced, and this by means of boiling dilute acids splits off hydroxylamine and is converted into flavonol—

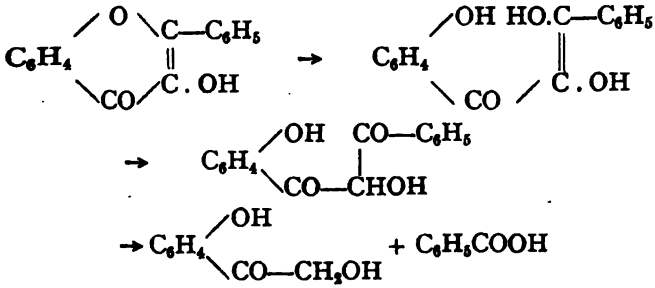


Flavonol crystallises from alcohol in yellow needles, melting-point 167—170°. When warmed with aqueous sodium hydroxide it forms a yellow liquid, and on cooling the sodium salt separates in the form of yellow needles. Its solution in sulphuric acid exhibits an intense violet fluorescence. *Acetylflavonol*, colourless needles, melts at 110—111°.

According to Auwers and Müller (Ber., 1908, 41, 4233) benzylidenecoumaranones can be converted into flavonols. Thus benzylidene 4 methylcoumaranone dibromide when treated with potassium hydroxide gives 2 methylflavonol. The reaction may be thus expressed :—



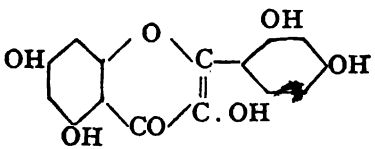
The hydrolysis of flavonol into *o*-hydroxybenzoylcarbinol and benzoic acid may be expressed by the following equations :—



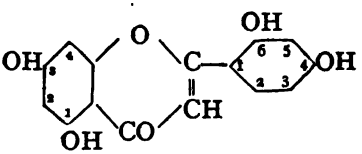
and this reaction, which is typical of the behaviour in these circumstances of the whole series of these compounds, has in general been employed to ascertain their structure. It is best effected by digesting the fully methylated flavonols with boiling alcoholic potash for some hours, for owing to the occurrence of secondary reactions it cannot be satisfactorily carried out with the unmethylated compounds.

For the synthesis of numerous flavonols, many of which occur naturally, v. Kostanecki and his co-workers have employed as a general method that found serviceable for the preparation of flavonol itself, and many instances of this are given in the sequel. The flavonols, with the exception of morin, which curiously enough is colourless, are yellow crystalline substances, soluble in alkaline solutions with a yellow colour, and yield with ease in the presence of acetic acid orange crystalline oxonium salts. According to Perkin, whereas as a rule hydroxyflavones are not oxidised by air in alkaline solution and can be precipitated therefrom unchanged by acids, flavonols on the other hand are readily decomposed in this manner with the formation of water-soluble products.

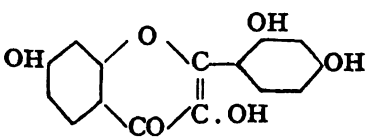
Interesting is the fact that though certain colouring matters of this group do not possess two hydroxyls in the ortho-position relatively to one another, they are nevertheless strong dyestuffs, and of these the tetrahydroxyflavonol morin may be taken as an example—



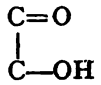
That this peculiarity arises from the presence of the pyrone hydroxyl is evident if the structure of morin is compared with the lotoflavone of Dunstan and Henry (*loc. cit.*)—



the tinctorial properties of which are exceedingly feeble. It seemed possible that this dyeing effect was to be attributed to the fact that this compound contains the hydroxyl (1) in the peri-position to the chromophore and which is present in most of the natural dyes of this group. Such a suggestion, however, became untenable on the synthesis of resomorin—

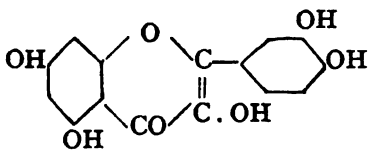


by Bonifazi, v. Kostanecki, and Tambor (Ber., 1906, 39, 86), which dyes the same shades as morin but does not contain the peri-hydroxyl in question. Evidently therefore the tinctorial properties of these hydroxy flavonols can only be accounted for by their possession of the grouping



the effect of which is considerably strengthened by the presence of hydroxyls in other positions in the molecule, and this has received support from the observation of v. Kostanecki and Szabránski that flavonol itself dyes on aluminium mordant a pale yellow shade. Though ortho-hydroxyl groups are not essential to the dyeing property of hydroxyflavonols, their presence, at least in certain positions, has considerable influence, not only in deepening the tone, but also in reddening the shade. Thus, whereas morin dyes bright yellow shades, quercetin (1)

(1)



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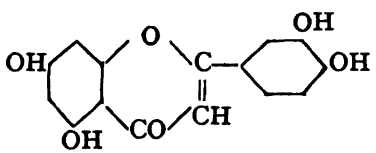


gives a brown-orange shade on aluminium mordant, and the effect of the pyrone hydroxyl is very evident on comparing quercetin with luteolin (2) which gives in the same way only a bright yellow colour. A multiplication of hydroxyls does not effect any general alteration of shade given by these compounds, as is so well known to take place in the anthraquinone group, and this affords support to the theory of Watson previously mentioned.

The shades given by the flavonols are not so fast to light as those given by the flavone luteolin, and this may arise in part owing to the greater susceptibility of their salts (or lakes) to oxidation. In this respect they vary again among themselves, quercetin being a somewhat faster colour than fisetin, and morin than quercetin.

On the other hand, the character of the shade given by the natural dyestuff varies in tone, as to whether the colouring matter is present as glucoside or in the free condition. Thus in dyeing with quercitron bark, quercitrin and not quercetin is the dyestuff, whereas in old fustic no glucoside is present, and the tinctorial effect is due to morin itself. The shade again given by a glucoside is naturally dependent on the position of the sugar nucleus, and thus the quercetin glucoside, quercimeritrin (see Cotton Flowers) has quite distinct properties in this respect from quercitrin itself. Again, a glucoside may be almost devoid of tinctorial property, as in the case of the kaempferol glucoside robinin and the alizarin glucoside ruberythric acid. The idea formerly held that glucosides in general were not true dyestuffs, and that during the dyeing operation by the action of the mordant they were hydrolysed with production of the colour lake of the free colouring matter, is incorrect. This evidently arose from the fact that in certain of these dyestuffs, as, for instance, madder and Persian berries, the glucoside is accompanied by its specific enzyme, which in case the temperature of the dye-bath is gradually raised from the cold upwards, effects the hydrolysis of the glucoside before the dyeing operation has really commenced.

In the following pages the natural dyestuffs containing flavonols, or their glucosides, are as far as possible arranged as to the number of hydroxyls present in the colouring matter, commencing with those which contain least. As, however, in many plants more than one flavonol is present, it has obviously not been possible to adhere strictly to this method of classification.

Galanga Root.

Galanga root is the rhizome of *Alpinia officinarum* (Hance) and is a native of China. It is employed in the form of a decoction as a remedy for dyspepsia.

Galanga root was first examined by Brandes (Arch. Pharm., (2), 19, 52), who isolated from it a substance which he named kaempferide, but this, according to Jahns (Ber., 1881, 14, 2385), was a mixture of three substances, kaempferide, alpinin, and galangin. The subject was later examined by Gordin (Dissert., Berne, 1897), and by Ciamician and Silber (Ber., 1899, 32, 861) and Testoni (Gazzetta, 1900, 30, ii., 327), and it is now clearly demonstrated that galanga root contains kaempferide, galangin, and galangin monomethylether. According to Testoni, the alpinin of Jahns is a mixture of galangin and kaempferide.

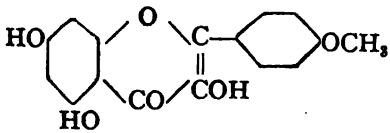
Kaempferide, $C_{16}H_{12}O_6$, consists of yellow needles, melting-point

227—229°, soluble in alkaline solutions with a yellow colour. Sulphuric acid gives a blue fluorescent yellow solution.

Triacetylkaempferide, $C_{16}H_9O_6(C_2H_3O)_3$, colourless needles, melting-point 193—194° (Ciamician and Silber and Testoni) (compare also Jahns), *tribenzoylkaempferide*, $C_{16}H_9O_6(C_7H_5O)_3$, melting-point 177—178° (Testoni), *kaempferide diethylether*,

$$C_{16}H_{10}O_6(OC_2H_5)_2$$

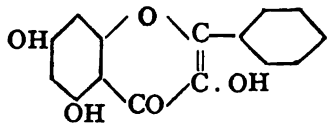
(Testoni), yellow needles, melting-point 137—139°, and *dibromkaempferide*, $C_{16}H_{10}Br_2O_6$, yellow needles, melting-point 224—225° (decomp.) (Jahns) have been prepared. In the presence of acetic acid, kaempferide yields, by means of mineral acids, yellow crystalline compounds, and alcoholic potassium acetate gives *monopotassium kaempferide*, $C_{16}H_{11}O_6K$, H_2O, yellow needles, which is decomposed by boiling water (Perkin and Wilson, Chem. Soc. Trans., 1903, 83, 136). Kaempferide is in reality *kaempferol monomethylether* (v. Kostanecki and Rozycki, Ber., 1891, 24, 3723)—



For a detailed description of kaempferol see *Delphinium consolida*.

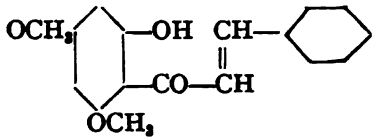
Galangin, $C_{15}H_{10}O_5$, the second constituent of galanga root, crystallises in yellowish-white needles, melting-point 214—215°, soluble in alkaline solutions with a yellow colour. With acetic anhydride, it gives a *triacetyl* derivative, $C_{15}H_7O_5(C_2H_3O)_3$, melting-point 140—142° (Jahns), and by means of methyl iodide a *dimethylether*, $C_{15}H_8O_3(OCH_3)_2$, melting-point 142°.

Galangin gives crystalline compounds with mineral acids in the presence of acetic acid, and reacts with alcoholic potassium acetate, yielding *monopotassium galangin*, yellow needles (Perkin and Wilson). When fused with alkali, *phloroglucinol* and *benzoic acid* are obtained. Galangin is a *dihydroxyflavonol*—



and has been synthesised by v. Kostanecki and Tambor (Ber., 1899, 32, 2260), by a series of reactions similar to those employed in the preparation of kaempferol.

2-Hydroxy-4 : 6-dimethoxychalkone—

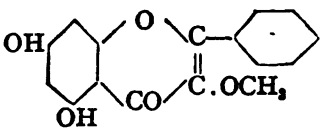


was converted into the corresponding flavanone, and the latter into its *iso*nitroso derivative. This compound, on boiling with dilute sulphuric acid, gave 1 : 3-dimethoxyflavonol which, when heated with hydriodic acid, was transformed into galangin. Galangin dyes with mordanted woollen cloth the following shades :—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Olive-yellow.	Yellow.	Lemon-yellow.	Deep olive.

Galangin monomethylether, $C_{15}H_9O_4(OCH_3)$, was first isolated from galanga root by Testoni (*loc. cit.*). It crystallises from methyl alcohol in bright yellow prisms, melts at about 300°, and dissolves in strong alkaline solutions with a yellow colour. *Diacetylgalangin monomethylether*, $C_{16}H_{10}O_5(C_2H_3O)_2$, forms yellowish-white leaflets, melting at 175—176°.

When air is aspirated through an alkaline solution of galangin monomethylether, it is oxidised with formation of *benzoic acid* and *phloroglucinol* (Perkin and Allison), and therefore possesses the constitution—



Delphinium consolida.

Delphinium consolida is a common European plant belonging to the Larkspur family; its name refers to its powers, real or imaginary, of healing or consolidating wounds. The blue flowers were examined by Perkin and Wilkinson (Chem. Soc. Trans., 1902, 81, 585) to determine if these yield the same colouring matters as those previously isolated from the flowers of the *D. zalil* (*ibid.*, 1898, 73, 267). The presence of kaempferol only could, however, be detected. For its isolation an aqueous extract of the flowers was digested at the boiling-point with addition of sulphuric acid, and the brown resinous product which separated on keeping, extracted with alcohol and the extract evaporated to a small bulk. Addition of ether to this solution caused the precipitation of resinous impurity, and on evaporating

the ethereal liquid a semi-crystalline residue of the crude colouring matter was obtained. The product was crystallised from dilute alcohol, converted into acetyl derivative, and this after purification retransformed into colouring matter in the usual manner. The yield was approximately 1 per cent.

Kaempferol, $C_{15}H_{10}O_6$, consists of yellow needles, melting-point 276—277°, soluble in alkaline solutions with a yellow colour. These liquids on exposure to air are slowly oxidised with development of a brown tint.

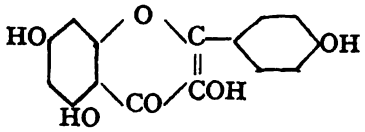
Tetra-acetylkaempferol, $C_{15}H_6O_6(C_2H_3O)_4$, when crystallised from methyl alcohol forms colourless needles, and when heated commences to melt at 116° and becomes completely fluid at 120°. On further heating, however, gradual solidification ensues and the product subsequently melts at 181—182°. This peculiarity of acetylkaempferol, which is not apparent when the substance is crystallised from ordinary alcohol, affords a convenient method for its detection.

Tribromkaempferol, $C_{15}H_7Br_3O_6$, forms yellow needles, melting-point 257—277°; *kaempferol sulphate*, $C_{15}H_{10}O_6H_2SO_4$, orange-red needles; *kaempferol hydriodide*, $C_{15}H_{10}O_6HI$, needles, and *monopotassium kaempferol*, $C_{15}H_9O_6K$, orange-yellow prismatic needles.

Kaempferide, a monomethyl ether of kaempferol, exists in Galanga root, and a similar compound, apparently distinct from this latter, has been isolated from the berries of the *Rhamnus catharticus*. The glucosides at present known of kaempferol are *robinin*, which occurs in the flowers of the *Robinia pseudacacia*; *kaempferitrin*, found in the leaves of the *Indigofera arrecta*; and *kaempferin*, which has been isolated from senna (*loc. cit.*).

Fused with alkali, kaempferol gives *phloroglucinol* and *p-hydroxybenzoic acid.*

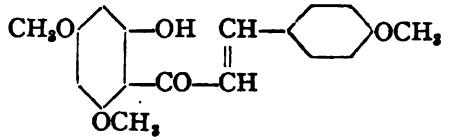
To kaempferol v. Kostanecki assigned the constitution of a *trihydroxyflavonol* (Ber., 1901, 34, 3723)—



and this compound has been synthesised by v. Kostanecki and Tambor (Ber., 1904, 37, 792).

2 *Hydroxy*. 4 : 6 : 4′ *trimethoxychalkone* (1) when digested with boiling dilute alcoholic sulphuric acid gives 1 : 3 : 4′ trimethoxy flavanone (2)—

(1)



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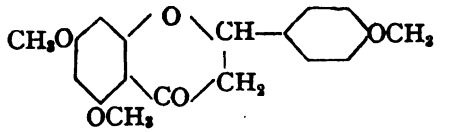
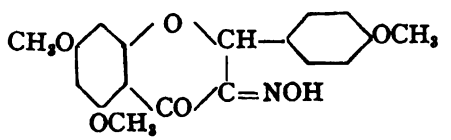


and the latter by means of amyl nitrite and hydrochloric acid is converted into *iso-nitroso* 1 : 3 : 4′ *trimethoxyflavanone* (3).

When a solution of this substance in acetic acid is boiled with 10 per cent. sulphuric acid 1 : 3 : 4′ *trimethoxyflavonol* (4) is produced, from which by the action of hydriodic acid *kaempferol* (5) is readily prepared—

(3)



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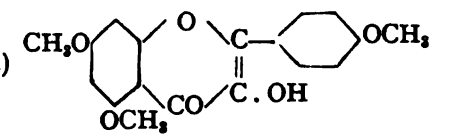

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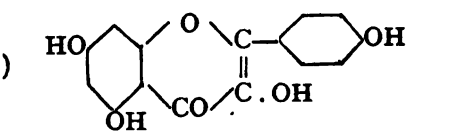


Kaempferol possesses well-defined dyeing properties, and gives with mordanted woollen cloth the following shades which closely resemble those given by morin (*loc. cit.*):—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Brownish-yellow.	Yellow.	Lemon-yellow.	Deep olive-brown.

It is also present in the *Impatiens balsamina* (Chantili Pass), the *Erythrina stricta* (vernacular name "Kon kathet"), (Perkin and Shulman, Chem. Soc. Proc., 1914, 30, 177), the berries of the *Rhamnus catharticus* (*loc. cit.*), and together with quercetin, both apparently as glucosides, in the flowers of the *Prunus spinosa* (Perkin and Phipps, Chem. Soc. Trans., 1904, 85, 56). For the separation

of the two colouring matters a fractional crystallisation from acetic acid was employed, kaempferol in these circumstances being the more sparingly soluble.

The Flowers of the Robinia pseudacacia. Robinin.

Robinin was first isolated from the flowers of the white Azalea by Zwenger and Dronke (Annalen, Supp., 1861, 1, 263), who considered that it was a glucoside of quercetin. Perkin (Chem. Soc. Trans., 1902, 81, 473) has shown that this is not the case.

To prepare the glucoside the flowers are exhausted with boiling alcohol, the solution concentrated by evaporation and poured into water. The mixture is extracted with ether, and the aqueous liquid distilled down to a small bulk. On standing, crystals of robinin separate, which are purified by crystallisation from water.

Robinin, according to Perkin, consists of pale yellow needles, sintering at 190° and melting at 196—197°, and when air-dried it possesses the formula $C_{33}H_{42}O_{20}$, $8H_2O$.

Boiling dilute sulphuric acid hydrolyses robinin with formation of kaempferol, 2 molecules of rhamnose and 1 of glucose, according to the following equation:—

$$C_{33}H_{42}O_{20} + 4H_2O = C_{15}H_{10}O_6 + 2C_6H_{14}O_6 + C_6H_{12}O_6$$

Schmidt (Chem. Zentr., 1901, ii., 121), who examined robinin at almost the same time, also obtained by its hydrolysis a colouring matter $C_{15}H_{10}O_6$, the acetyl compound of which melts at 182—183° (evidently kaempferol), and Waljascko (J. Russ. Phys. Chem. Soc., 1904, 36, 421), again, no doubt, also unaware of the communication of Perkin, terms this colouring matter $C_{15}H_{10}O_6$, H_2O, *robigenin*. Robinin he considered to possess the formula $C_{33}H_{40}O_{19} . 7\frac{1}{2}H_2O$, and the sugars that it yields by hydrolysis to consist of galactose (1 mol.) and rhamnose (2 mols.).

Robinin is a most interesting glucoside, and with the exception of xanthorhamnin is the only known substance of this class which yields three sugar nuclei. It is practically devoid of tinctorial property.

Interesting is the fact that whereas the bark of this plant contains *acacetin*, the monomethyl ether of the trihydroxyflavone, apigenin, its flowers yield the glucoside of the trihydroxyflavonol kaempferol. Whether the occurrence of distinct flavones in various portions of the same plant is exceptional or otherwise, has been little studied, and appears to have only been observed elsewhere in the cases of the

yellow cedar (*Rhodesphaera rhodanthema*), the leaves of which contain quercetin and the stem fisetin, and the Venetian sumach, the stem of which contains fisetin and the leaves myricetin.

Young Fustic.

Young fustic consists of the wood of the stem and larger branches of the *Rhus cotinus* (Linn.), a small tree which is a native of Southern Europe, and the West India Islands. It is a hard compact yellow wood, and is usually imported in small bundles or faggots. Within the last few years young fustic has almost disappeared from the market, not only on account of the artificial colouring matters, but because the shades it yields lack permanence, and the percentage of colouring matter it contains is small. The leaves of the *R. cotinus* constitute Venetian sumach, a tanning material which is employed to some extent in Italy and Southern Europe.

Fisetin, $C_{15}H_{10}O_6$, the colouring matter of young fustic, was first isolated by Chevreul ("Leçons de Chimie appliquée à la Teinture," A. ii., 150), who gave it the name "Fustin". Bolley (Schweiz. polyt. Zeitschr., 1864, 9, 22) considered that it was identical with quercetin, but Koch (Ber., 5, 285) maintained that fisetin was probably an aldehyde of quercetinic acid.

Schmid (Ber., 1886, 19, 1734), who carried out an exhaustive examination of this dyewood, obtained fisetin in a pure condition and proved that it was not identical with quercetin. He found that in addition to the free colouring matter, young fustic contains a glucoside of fisetin combined with tannic acid to which he gave the name of *fustin tannide*.

To prepare fisetin, Schmid (*loc. cit.*), and later Herzig (Monatsh., 12, 178), employed "cotinin" (*v. infra*), a commercial preparation of young fustic which is no longer on the market. According to Perkin and Pate (Chem. Soc. Trans., 1895, 67, 648), fisetin is readily isolated from the dyewood as follows:—

Young fustic is extracted with boiling water, and the extract treated with lead acetate solution. The lead compound of the colouring matter is collected, made into a thin paste with water, and in a fine stream run into boiling dilute sulphuric acid. After removal of lead sulphate the dark-coloured filtrate, on cooling, deposits a semi-crystalline brownish mass, which is collected and purified by crystallisation from dilute alcohol.

Schmid assigned the formula $C_{22}H_{16}O_9$ to fisetin, but it was found by Herzig that the analyses agreed equally well with $C_{15}H_{10}O_6$, and that

this formula was correct was supported by the work of Perkin and Pate (*loc. cit.*), who gave to fisetin sulphate the formula—

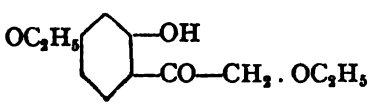
$$C_{15}H_{10}O_6 . H_2SO_4$$

Fisetin forms yellow needles, melting at above 360°, easily soluble in alcohol. Alkaline solutions dissolve it with a deep yellow colour which, on exposure to air, gradually changes to brown; with alcoholic ferric chloride it gives a deep green coloration, and with lead acetate a bright orange-red precipitate. *Tetra-acetylfisetin*, $C_{15}H_6O_6(C_2H_3O)_4$, melting-point 196—198°, crystallises in colourless needles, and the *benzoyl* derivative, $C_{15}H_6O_6(C_7H_5O)_4$, needles, melts at 180—181° (Perkin and Pate), (Schmid, 184—185°). Fisetin gives with mineral acids in the presence of acetic acid crystalline salts. *Fisetin sulphate*, $C_{15}H_{10}O_6 . H_2SO_4$, scarlet needles, *fisetin hydrobromide*, $C_{15}H_{10}O_6 . HBr$, orange needles, and *fisetin hydrochloride* have been prepared in this manner (Perkin and Pate). These compounds are readily decomposed by water. *Monopotassium fisetin*, $C_{15}H_9O_6K$, yellow needles (Perkin, Chem. Soc. Trans., 1899, 75, 433), is obtained from fisetin by means of alcoholic potassium acetate.

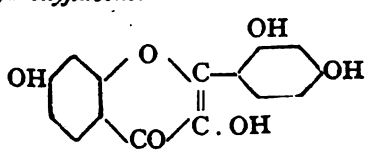
By fusion with alkali or oxidation of its alkaline solution by exposure to air fisetin gives *resorcinol* and *protocatechuic acid* (Herzig).

On ethylation with ethyl iodide fisetin is converted into *fisetin tetraethyl ether*, $C_{15}H_6O_2(OC_2H_5)_4$, colourless needles, melting-point 106—107°; the corresponding methyl derivative, $C_{15}H_6O_2(OCH_3)_4$, melts at 152—153°.

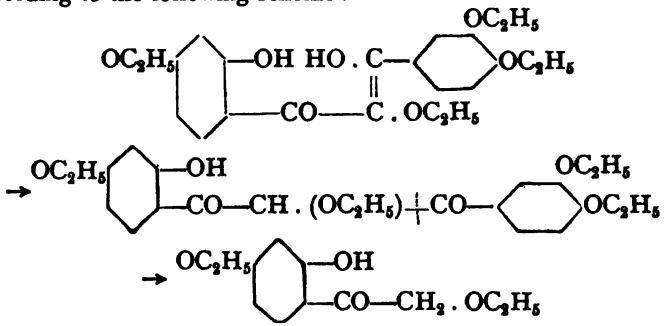
When fisetin tetraethyl ether is submitted to the action of boiling alcoholic potash it gives *protocatechuic acid diethyl ether*, and *fisetol diethyl ether* (Herzig), colourless needles, melting-point 42—44°. This latter compound, by oxidation with permanganate, is converted into the *monoethyl ether* of *resorcylic acid*, and the *monoethyl ether* of *resorcinolglyoxylic acid*, and consequently fisetol diethyl ether may be thus represented—



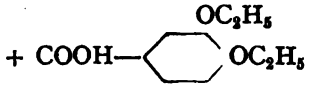
As a result of his investigation Herzig assigned to fisetin the constitution of a *trihydroxyflavonol*—



The tetraethyl derivative of this compound suffers hydrolysis according to the following scheme :—



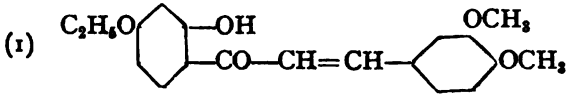
Fisetol diethyl ether.



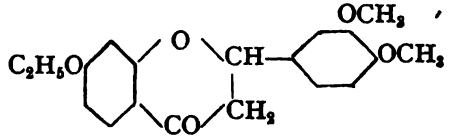
Protocatechuic acid diethyl ether.

Fisetin has been synthesised by v. Kostanecki, Lampe, and Tambor (Ber., 1904, 37, 784).

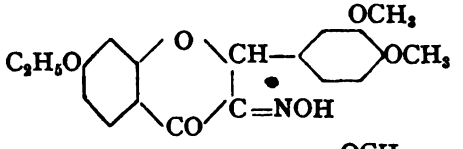
2-*Hydroxy*-4-*ethoxy*-3′ : 4′-*dimethoxychalkone* (1)—

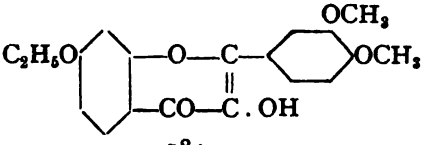


prepared by the condensation of resacetophenone monoethyl ether with veratric aldehyde, when digested with boiling dilute alcoholic sulphuric acid gives 3-ethoxy-3′ : 4′-dimethoxyflavanone (2)—



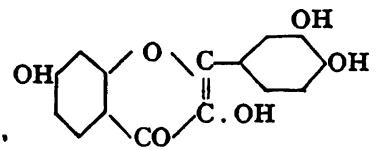
and this, when treated with amyl nitrite and strong hydrochloric acid in alcoholic solution, is converted into the *iso*nitroso compound (3)—





When boiled in acetic acid solution with 10 per cent. sulphuric acid this substance gives 3-ethoxy-3′-4′-dimethoxyflavonol (4), from which fisetin (5) is readily produced by the action of boiling hydriodic acid—

(5)



Fisetin is a strong colouring matter and gives shades which are almost identical with those produced by quercetin, rhamnetin, and myricetin. The colours given with wool mordanted with chromium, aluminium, and tin are, respectively, red-brown, brown-orange, and bright red-orange (Perkin and Hummel, Chem. Soc. Trans., 1896, 69, 1290).

The glucoside of fisetin, according to Schmid (*loc. cit.*), is prepared as follows: A boiling aqueous extract of young fustic is treated with lead acetate, the precipitate removed, the clear liquid freed from lead by means of sulphuretted hydrogen, and saturated with salt. The mixture is filtered, the filtrate extracted with ethyl acetate, and the extract evaporated. There is thus obtained a residue consisting of the crude fustin-tannide, which is purified by solution in water, precipitation with salt, and extraction with ethyl acetate.

Fustin tannide crystallises in long yellowish-white needles, which are easily soluble in water, alcohol, and ether. When heated it decomposes above 200°. If a solution of fustin tannide in hot acetic acid is treated with water, and allowed to stand for some time, colourless crystals of *fustin* are gradually deposited.

Fustin crystallises from water in yellowish-white needles, melting-point 218—219°, and when digested with boiling dilute sulphuric acid gives *fisetin* and a sugar, the nature of which has not been determined. The formula given to this glucoside $C_{58}H_{46}O_{23}$ by Schmid cannot be regarded as correct, in view of the fact that the true formula of fisetin is now known to be $C_{15}H_{10}O_6$.

Dyeing Properties of Young Fustic.—The colours derived from young fustic are all fugitive to light, hence this dyestuff has lost its importance. In silk dyeing it was formerly used for dyeing brown, the silk being mordanted with alum, and afterwards dyed with a decoction of young fustic, peachwood, and logwood. With the various metallic salts as mordants young fustic yields colours somewhat similar to those obtained from old fustic, the chromium colour is, however, much redder, being a reddish-brown, and the aluminium yellow is much

duller; stannous chloride on the contrary gives an incomparably more brilliant orange, not unlike that obtainable from flavin or from Persian berries (Hummel).

Fisetin is present also as glucoside in the wood of the yellow cedar, *Rhodosphacra rhodanthema*, and in the wood of the *Quebracho colorado* (*loc. cit.*).

The leaves of the *R. cotinus* contain myricetin.

Yellow Cedar.

The *Rhodosphacra rhodanthema* (Engl.) or yellow cedar, a tree growing to the height of 70 or 80 feet, is indigenous to the northern part of New South Wales.

The colouring matter of this dyewood is fisetin, which is readily isolated by the method described in connection with young fustic (Perkin, Chem. Soc. Trans., 1897, 71, 1194).

A second substance, $C_{36}H_{30}O_{16}$?, colourless needles, melting-point 215—217°, is also present in small amount, and may be identical with fustin, the glucoside of fisetin obtained from young fustic by Schmid (Ber., 1886, 19, 1755).

The shades given by the yellow cedar are slightly weaker and differ considerably from those given by young fustic (*Rhus cotinus*), although both contain the same colouring matter. Employing mordanted woollen cloth, the following distinctions are observed:—

	Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Young fustic . .	Reddish-brown	Orange	Orange-yellow	Brown-olive
Yellow cedar . .	Yellowish-brown	Brownish-yellow	Golden-yellow	Olive

and these may be due to varying amounts of the glucoside which is contained in both plants.

Quercitron Bark.

This important yellow dyestuff, the latest addition to the somewhat meagre list of commercial natural colouring matters, was discovered and introduced by Bancroft in 1775. In his "Philosophy of Permanent Colours" he states (ii., 113): "Quercitron bark is one of the objects of a discovery of which the use and application for dyeing are exclusively vested in me, for a term of years by an Act of Parliament in the twenty-fifth year of his present Majesty's reign".

Quercitron bark is the inner bark of a species of oak known as

Quercus discolor, Ait. (*Q. tinctoria*), which is a native of the Middle and Southern States of America. The tree in the south is described as being from 60 to 80 feet high, with a trunk from 6 to 10 feet in diameter; but in the north it does not attain to this size. In order to obtain the dyestuff the epidermis or exterior blackish coat of bark is usually removed by shaving and the inner portion then detached and ground. The product may be separated into stringy fibres and a light fine powder, the latter of which contains the principal portion of the colouring matter.

Quercitron bark and its preparations are still used to a considerable extent, although not so much as was formerly the case. This is not only due to the introduction of the artificial colouring matters, but because it has been supplanted for many purposes by the less costly old fustic.

Quercetin, $C_{15}H_{10}O_7$, the colouring matter of quercitron bark, has been the subject of numerous researches, and many of these unfortunately resulted in the publication of complicated and unsatisfactory formulæ. At an early stage it was ascertained that quercetin does not exist in the plant, at least to any extent in the free condition, but in the form of its glucoside *quercitrin*.

To prepare quercetin the following method devised by the late Sir W. H. Perkin, and employed by him for several years on the manufacturing scale, gives good results. Quercitron bark dust is macerated with moderately strong salt solution to remove gummy substances, filtered, and then extracted with dilute ammonia. The cold ammoniacal liquid is treated with a slight excess of hydrochloric acid, causing the separation of certain impurities in the form of a brown flocculent precipitate. This is removed, and the pale yellow acid solution of the glucoside is boiled for about thirty minutes. The glucoside is thus hydrolysed and almost chemically pure quercetin separates in the form of pale yellow needles, which are collected while the mixture is still warm and washed with water. It is readily soluble in alcohol, and dissolves in alkaline solutions with a yellow colour. With aqueous lead acetate it gives a bright orange-red precipitate, and with alcoholic ferric chloride a dark green colour.

The most important of the early investigations of quercetin was carried out by Liebermann and Hamburger (Ber., 12, 1178), who assigned to it the formula $C_{24}H_{16}O_{11}$, and to quercitrin the formula $C_{36}H_{28}O_{20}$. Herzig (Monatsh., 5, 72; 6, 863; 9, 537; 12, 172; 14, 53; 15, 697), who made an elaborate series of researches on this subject, at first adopted this formula. Subsequently it was ascertained that quercetin was in reality $C_{15}H_{10}O_7$, and this received

support by the examination of its compounds with mineral acids (Perkin and Pate, Chem. Soc. Trans., 1895, 67, 647).

When quercetin is fused with alkali, it gives *protocatechuic acid* and *phloroglucinol*, and if its alkaline solution is oxidised with air, the same products are obtained. By the more gentle action of the alkali, Hlasiwetz and Pfaundler (Jahres., 1864, 561) obtained certain intermediate products of the hydrolysis, *paradiscetin*, $C_{15}H_{10}O_6$, yellow needles, *quercetic acid*, $C_{15}H_{10}O_7$, colourless needles, and *quercimeric acid*, $C_8H_6O_5$, H_2O, colourless crystals. Herzig and others who have reinvestigated this decomposition have been unable to obtain the substances of Hlasiwetz and Pfaundler, and if these compounds are in reality chemical individuals, it seems likely that their formation was due to the action of some special impurity contained in the alkali employed by these chemists.

On acetylation quercetin gives a *penta-acetyl compound*,

$$C_{15}H_5O_7(C_2H_3O)_5,$$

colourless needles, melting at 191—195°, but on methylation with methyl iodide the *tetramethyl ether*, $C_{15}H_6O_3(OCH_3)_4$, long yellow needles, melting-point 156—157° (H.), is produced. A free hydroxyl group is thus still present in this compound, and it yields with alcoholic potash a bright yellow salt decomposable by water, and a *monoacetyl* derivative, $C_{15}H_5O_3(C_2H_3O)(OCH_3)_4$, needles, melting-point 167—169° (H.). The *ethylation* product, $C_{15}H_6O_3(OC_2H_5)_4$, yellow needles, melting-point 120—122°, is similarly constituted, and gives the *acetyl* compound $C_{15}H_5O_3(OC_2H_5)_4(C_2H_3O)$, melting-point 151—153°.

When heated with alcoholic potash, quercetin tetramethyl ether forms *veratric acid* and a syrupy phloroglucinol derivative (H.), and this latter has been shown (Perkin and Allison, Chem. Soc. Trans., 1902, 81, 471), by means of its disazobenzene derivative, to consist of *phloroglucinol monomethyl ether*. Quercetin tetraethyl ether exhibits a similar behaviour.

The following is a list of the more important derivatives of quercetin: *Dibromquercetin*, $C_{15}H_8Br_2O_7$, yellow needles, melting-point 233—235° (H.); *acetyl dibromquercetin*, $C_{15}H_3Br_2O_7(C_2H_3O)_5$ (H.); *dibromquercetin tetraethyl ether*, yellow needles, melting-point 169—173°; *quercetin triphenylcarbamide*,

$$(OH)_2 . C_{15}H_5O_5(OCO . NH . C_6H_5)_3$$

(Tesmer, Ber., 1885, 18, 2609); *triacetyl quercetin*, $C_{15}H_7O_7(C_2H_3O)_3$, colourless needles, melting-point 167—169°; *tetra-acetylquercetin*, $C_{15}H_6O_7(C_2H_3O)_4$, melting-point 193—194° (Perkin, Chem. Soc. Trans., 1899, 75, 449); *benzoylquercetin*, $C_{15}H_5O_7 . (C_7H_5O)_5$, melting-

point 239° (Dunstan and Henry, Chem. Soc. Trans., 1898, 73, 219). With mineral acids in the presence of acetic acid, quercetin gives *quercetin sulphate*, $C_{15}H_{10}O_7 . H_2SO_4$, *quercetin hydrobromide*,

$$C_{15}H_{10}O_7 . HBr,$$

quercetin hydrochloride, $C_{15}H_{10}O_7 . HCl$, and *quercetin hydriodide*,

$$C_{15}H_{10}O_7 . HI,$$

which crystallise in orange needles and are decomposed by cold water (Perkin and Pate). *Monopotassium quercetin*, $C_{15}H_9O_7K$, and *monosodium quercetin*, $C_{15}H_9O_7Na$, orange needles, are produced by the action of alcoholic potassium and sodium acetates (Perkin, Chem. Soc. Trans., 1899, 75, 438). *Aminoquercetin*, $C_{15}H_4O_2(OH)_5NH_2$, pale yellow needles, has been obtained by Watson (Chem. Soc. Proc., 1911, 27, 163) by the action of hydriodic acid (1·7) on aminopentamethylquercetin. The *hydrochloride*, $C_{15}H_9O_7 . NH_2 . HCl$, yellow needles, the *hydriodide*, *sulphate*, and *acetyl* derivative, colourless rhombs, melting point 151—153°, are also described. Aminoquercetin dyes mordanted wool browner and deeper colours than quercetin itself.

Quercetin is a strong dyestuff, and gives with mordanted wool the following shades, which are almost identical with those produced by fisetin:—

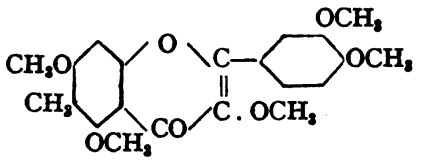
Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Red-brown.	Brown-orange.	Bright orange.	Olive-black.

The suggestion that quercetin was probably *hydroxyfisetin* is due in the first place to Herzig, and this has been substantiated by the synthesis of this colouring matter (see below).

Though Waliascko (Arch. Pharm., 1904, 242, 225) by means of methyl sulphate succeeded in preparing *pentamethyl quercetin*,

$$C_{15}H_5O_2(OCH_3)_5,$$

colourless needles, melting-point 148°, it had long been considered that the full methylation of quercitin could not be effected with methylic iodide, on account of its possession of an hydroxyl in the ortho-position to the carbinol group. In 1913, however, it was shown by Perkin (Chem. Soc. Trans., 103, 1632) that if a methyl alcoholic solution of quercetin is diluted with an excess of methyl iodide, and boiled with gradual addition of alcoholic potassium hydroxide solution pentamethyl quercetin can be readily prepared. At the same time a small amount of *methyl quercetin pentamethyl ether*, $CH_3 . C_{15}H_4O_2(OCH_3)_5$, melting-point 213—215°, probably



and *methylquercetin tetramethyl ether*, $CH_3 . C_{15}H_5O_3(OCH_3)_4$, colourless needles, melting-point 184—185°, the *monacetyl* derivative of which melts at 178—180°, were produced. Employing ethyl iodide in a similar manner *quercetin pentaethyl ether*, $C_{15}H_5O_2(OEt)_5$, colourless prismatic needles, melting-point 116—118°, is formed in excellent yield (Chem. Soc. Proc., 1912, 28, 329).

From quercetin pentamethyl ether Watson (Chem. Soc. Proc., 1911, 27, 163) has prepared the following compounds: *Nitropentamethylquercetin*, $C_{15}H_4O_2(OCH_3)_5 . NO_2$, yellow needles, melting-point 202—204°; *aminopentamethylquercetin*, $C_{15}H_4O_2(OCH_3)_5 . NH_2$, colourless prisms, melting-point 200-202°; *pentamethylquercetin hydrobromide*, $C_{20}H_{20}O_7 . HBr$; *hydrochloride*, $C_{20}H_{20}O_7 . HCl$; *sulphate*, $C_{20}H_{20}O_7 . H_2SO_4$; *nitrate*, $C_{20}H_{20}O_7 . HNO_3$, yellow needles; *trinitropentamethylquercetin*, $C_{15}H_2O_2(OCH_3)_5(NO_2)_3$, melting-point 190—205°; *dibrompentamethylquercetin*, $C_{15}H_3O_2 . Br_2 . (OCH_3)_5$, colourless prisms, melting-point 173—175°; *dibrompentamethylquercetin hydrobromide*, $C_{20}H_{18}O_7 . Br_2 . HBr$; *dibromnitropentamethylquercetin*,

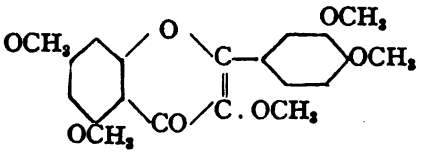
$$C_{15}H_2O_2Br_2 . (OCH_3)_5 . NO_2,$$

yellow rhombs, melting-point 173—175°; *pentamethylquercetin diazonium chloride*, $C_{15}H_4O_2 . (OCH_3)_5 . N_2 . Cl$, yellow needles; *sulphate*, yellow needles, and *pentamethylquercetin-azo-β-naphthol*,

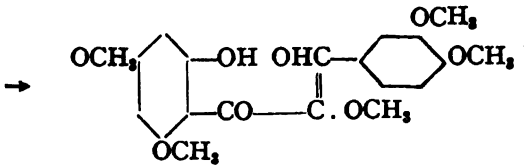
$$C_{15}H_4O_2(OCH_3)_5 . N_2 . C_{10}H_6OH$$

The benzopyranol derivatives obtained by Watson from quercetin are described in the section devoted to that group.

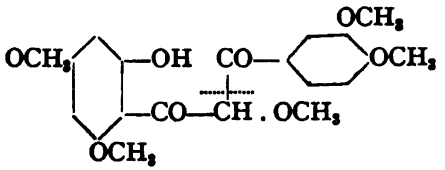
Pentamethylquercetin, when hydrolysed with alcoholic potash (Herzig, Ber., 1909, 42, 155), gives together with *veratric acid* the *methoxy derivative of the fisetol dimethyl ether*, which is obtained (Monatsh., 1891, 12, 187) by the hydrolysis of fisetin tetramethyl ether. The reaction may be expressed as follows:—



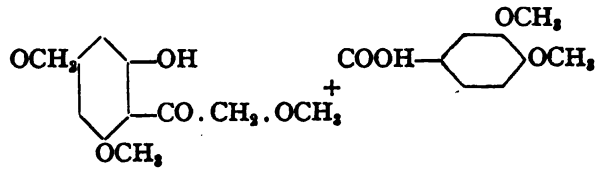
Quercetin pentamethyl ether.



Intermediate compound.

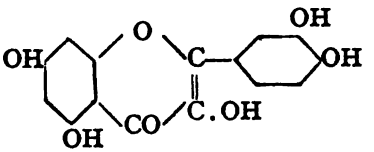


Hydroxypentamethoxybenzoylacetophenone.

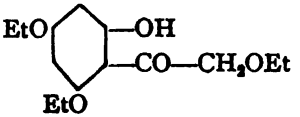


Methoxyfisetol dimethyl ether.

and affords a clear proof of the flavonol constitution of quercetin—



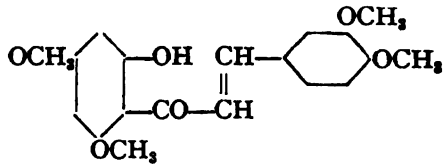
In the same way methyl quercetin pentamethyl ether gives veratric acid and *methoxy methyl fisetol dimethyl ether*, fine needles, melting-point 148—149°, whereas quercetin pentaethyl ether forms *hydroxy fisetol triethyl ether*—



which melts at 96—97° (Perkin, *loc. cit.*).

Quercetin has been synthesised by v. Kostanecki, Lampe, and Tambor (Ber., 1904, 37, 1402) by a series of reactions similar to those which had been successfully employed for the preparation of fisetin. The starting-point of the synthesis was 2 hydroxy, 4, 6, 3′ : 4′ tetramethoxychalkone, and the following formulæ indicate the procedure adopted (compare fisetin) :—

(1)



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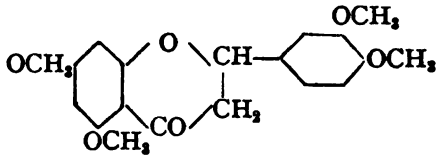

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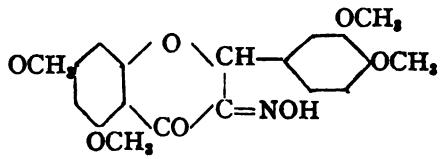

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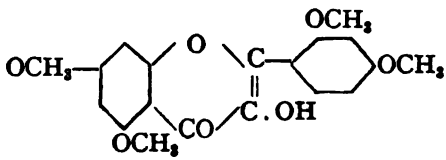

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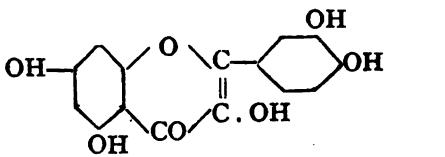
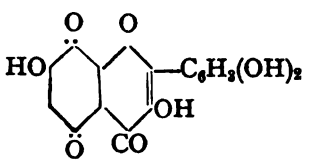
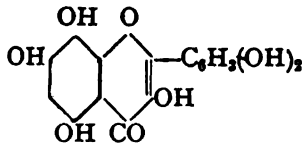


According to Nierenstein and Wheldale (Ber., 1911, 44, 3487), quercetin by oxidation with chromic acid is converted into *quercetone*, deep red needles (melting-point above 300°). This they considered to resemble anthocyanin in that it dissolved in alkali hydroxides with a blue and in concentrated sulphuric acid with a red coloration. This latter, however, is not a reaction of anthocyanins. It possesses the formula



(compare v. Kostanecki and Tambor, Ber., 1902, 35, 1869; *ibid.*, 1906, 39, 4012), and when heated with zinc-dust and acetic anhydride it yields the acetyl derivative (amorphous) of *hydroxyquercetin*—



This pentahydroxyflavonol, yellow needles, melts at 352—355°, and gives a colourless *hexamethyl derivative*, melting-point 147—149°.

Quercitrin, the glucoside of quercetin, was first isolated from quercitron bark by Chevreul, and has been examined by numerous chemists. The method usually employed for the preparation of this substance is that devised by Zwenger and Dronke (Annalen, Suppl., 1, 267), and this was subsequently utilised by Liebermann and Hamburger (Ber., 12, 1179).

Quercitron bark is extracted with 5—6 times its weight of boiling 50 per cent. alcohol, the extract evaporated to one-half, and treated with a little acetic acid, followed by lead acetate solution. The precipitate is removed, sulphuretted hydrogen is passed through the filtrate, and after removal of lead sulphide the clear liquid is evaporated to dryness. The residue is dissolved in a little hot alcohol, the solution treated with water and the crude quercitrin which separates on cooling is purified by repeated crystallisation from water.

A very convenient source of quercitrin is *yellow flavine* (Perkin, private communication), which consists almost entirely of this substance, and is usually free from quercetin. A hot aqueous extract of this material gives, on cooling, a crystalline precipitate of the glucoside, and this by recrystallisation from water with the aid of animal charcoal is readily obtained pure.

Quercitrin crystallises in very pale yellow, almost colourless leaflets, insoluble in cold water, somewhat readily so in alcohol. Aqueous lead acetate gives a bright yellow precipitate. The generally accepted formula for quercitrin was $C_{21}H_{22}O_{12}$, $2H_2O$ (Herzig, Monatsh., 14, 53), and its hydrolysis with acids into rhamnose (Hlasiwetz and Pfaundler) and quercetin was usually expressed as follows:—

$$C_{21}H_{22}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{14}O_6$$

According to C. W. Moore, however (Chem. Soc. Proc., 1910, 26, 183), the true composition of quercitrin is $C_{21}H_{20}O_{11}$, $2H_2O$, and the equation representing its hydrolysis should be as follows:—

$$C_{21}H_{20}O_{11} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$$

When air-dried quercitrin melts at 182—185°, and in the anhydrous condition at 250—252°.

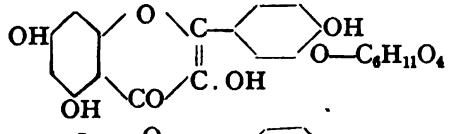
It was formerly considered that the glucosides (colouring prin-

ciples) were hydrolysed during the dyeing operation, and that the shades thus obtained were due not to the glucosides, but to the free colouring matters. This in certain cases is correct, especially when the plant contains an enzyme capable of effecting the hydrolysis; but on the other hand, in many cases the glucoside is itself the colouring matter and directly responsible for the dyeing effect. Quercitrin is an instance in point (Perkin, Chem. Soc. Trans., 1902, 81, 479), and gives upon mordanted fabrics shades which are distinct from those of quercetin itself.

	Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Quercitrin	Full brown-yellow.	Full golden-yellow.	Lemon-yellow.	Deep olive.
Quercetin	Red-brown.	Brown-orange.	Bright orange.	Olive black.
Kaempferol	Brown-yellow.	Yellow.	Lemon-yellow.	Deep olive-brown.

In dyeing property quercitrin very closely resembles kaempferol, and, indeed, differs but little from morin (old fustic) and luteolin (weld) in this respect. It was thus probable, according to Perkin (*loc. cit.*), that the constitution of the glucoside is to be represented by one of the two following formulæ:—

(1).



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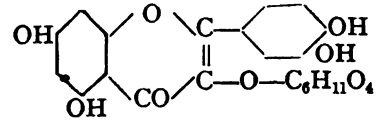
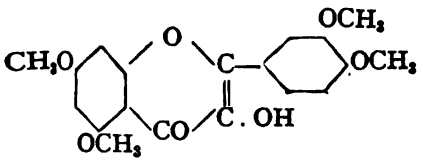
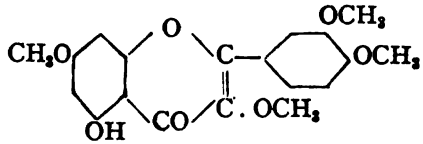


By the action of diazomethane on quercitrin (Herzig and Schönbach, Monatsh., 1912, 33, 673), the free hydroxyl groups of the quercetin nucleus are readily methylated, and subsequently one methyl enters the rhamnose nucleus giving *pentamethylquercitrin*, a light yellow amorphous powder. This when hydrolysed by dilute acid gives colourless *tetramethylquercetin*, $C_{15}H_6O_3(OCH_3)_4$, crystallising in needles, melting-point 195—198°, the *acetyl compound* of which melts at 160—163°. Quercetin with diazomethane yields also this colourless tetramethyl compound, in addition to quercetin pentamethyl ether (Herzig and Böttcher, *ibid.*, 683). Colourless quercetin tetramethyl ether is identical with the 1 : 3 : 3′ : 4′ tetramethoxyflavonol of v. Kostanecki, Lampe, and Tambor (Ber., 1904, 37, 1402)—



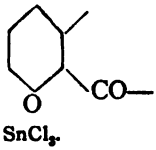
and consequently it is evident that quercitrin may be represented by the second formula given above.

Yellow quercetin tetramethyl ether—



according to these authors, cannot be further methylated with diazomethane, but the immunity of the ortho-hydroxyl to this reagent is only exerted when the other hydroxyls are substituted.

Pfeiffer (Ber., 1911, 48, 1269) has shown, in the case of hydroxy ketones, that the hydroxyl in the ortho-position relatively to the carbonyl group reacts with stannic chloride in benzene solution to form a substitution compound of the type—



whereas the hydroxyls in other positions give only addition products. According to Herzig and Böttcher yellow and colourless quercetin tetramethyl ethers obey this rule, the former giving a substitution and the latter an addition product.

The colours given by quercitrin are somewhat faster than those derived from quercetin.

Commercial Preparations.

FLAVIN.

This is the most important commercial preparation of quercitron bark; it seems to have been first imported into this country from America. The details of its manufacture have been guarded with much secrecy, and analyses of commercial samples show that different methods have been adopted by different makers. Some specimens consist essentially of quercitrin, and are known as *yellow* flavin, whilst others contain only quercetin, and are known as *red* flavin. The

former have probably been prepared by merely extracting the bark with water and high-pressure steam, or, as it is said, with steam only at a temperature of 102—103°.

The best qualities of flavin are those in which the colouring matter is present as more or less pure quercitrin, and entirely free from woody fibre. Red flavin is prepared by rapidly extracting the powdery portion of rasped quercitron bark with ammonia or other alkali, and boiling the solution with sulphuric acid. The precipitate thus produced is ultimately collected, washed with cold water till free from acid, and finally dried. Flavin of this character has about sixteen times the tinctorial value of quercitron bark. It is not very soluble, but it yields with aluminium, and especially with tin mordants, much more brilliant colours than quercitron bark itself.

Patent Bark.

Patent bark, or "commercial quercetin," is a preparation of quercitron bark analogous to the garancin made from madder. It is manufactured in a similar manner, viz. by boiling, for about two hours, 100 parts finely ground quercitron bark, 300 parts water, and 15 parts concentrated sulphuric acid. The product is collected on a filter, washed free from acid, and dried. The yield is about 85 per cent. of the bark employed, while its colouring power is much greater. It seems to have been first manufactured in 1855 by Leeshing.

Bark-liquor.

Bark-liquor is simply an aqueous extract of quercitron bark, and is sold with a specific gravity of 1·66—1·255.

Application.—Quercitron bark, patent bark, and bark extracts have been largely employed by the calico and woollen printer. The latter are used in the preparation of steam-yellows, olives, chocolates, etc., in conjunction with aluminium, tin, chromium, and iron mordants. The former at one time found employment in conjunction with garancin for the production of various compound shades, e.g. chocolate, dull red, orange, etc. Now they may be used in a similar manner along with alizarin. When used alone, quercitron bark and patent bark give, with aluminium mordant yellow, with tin orange, with chromium olive-yellow, with iron greenish-olive colours.

Flavin is chiefly serviceable in wool dyeing for the production, in single-bath, of bright yellow and orange, fast to milling, and was at one time largely used along with cochineal to obtain a bright scarlet. The mordant employed is stannous chloride and oxalic acid or cream of tartar.

On cotton all the quercitron colours are but moderately fast to light; on wool and silk the chromium, copper, and iron colours are fairly fast, whereas the aluminium and tin colours are only moderately so.

Glucosides of Quercetin.

RUTIN.

Rutin was discovered by Weiss (Chem. Zentr., 1842, 305) in the leaves of a rue (*Ruta graveolens*, Linn.), and was subsequently isolated from capers (*Capparis spinosa*, Linn.) by Rochleder and Hlasiwetz (Ann. Chem. Pharm., 82, 196), and by Schunck (Manchester Memoirs, 1858, 2 Ser., 155, 122) from buckwheat (*Fagopyrum esculentum*, Moench.). Whereas Hlasiwetz (Ann. Chem. Pharm., 96, 123) came to the conclusion that rutin was identical with quercitrin, it was shown by Zwenger and Dronke (*ibid.*, 123, 145) that this could not be the case, because on hydrolysis rutin gives quercetin and two molecules of sugar. Schunck (Chem. Soc. Trans., 1888, 53, 262; 67, 30) considered that the formula of rutin is $C_{27}H_{32}O_{16}$, $2H_2O$, and that on hydrolysis it is converted into *quercetin* and 2 molecules of rhamnose, $C_{27}H_{32}O_{16} + 3H_2O = C_{15}H_{10}O_7 + 2C_6H_{14}O_6$. Rutin, moreover, was identical with the *sophorin*, which Foerster (Ber., 15, 214) had isolated from the *Sophora japonica*.

It has been shown by Schmidt (Chem. Zentr., 1901, ii., 121) that by the hydrolysis of rutin glucose is also produced, the formula of this substance being therefore $C_{27}H_{30}O_{16}$.

$$C_{27}H_{30}O_{16} + 3H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6 + C_6H_{14}O_6$$

Rutin forms pale yellow glistening needles, sparingly soluble in water, and is said to melt above 190°. With alcoholic potassium acetate it gives a bright yellow *monopotassium salt* (Perkin, Chem. Soc. Trans., 1899, 75, 440).

According to Schmidt, *violaquercitrin* (violarutin) is identical with rutin (*ibid.*, 1908, 246, 274), and Perkin (*ibid.*, 1910, 97, 1776) has shown that *osyritin* (*Colpoon compressum*, Berg.) (*Osyris compressa*) (*ibid.*, 1902, 81, 477) and *myrticolorin* (*Eucalyptus macrorhyncha*, F. Muell.) (Smith, *ibid.*, 1898, 73, 697) in reality consist of this substance (*loc. cit.*).

The dyeing properties of rutin are similar to, though weaker than those of quercitron bark. The following shades are given on mordanted woollen cloth :—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Brown-yellow.	Full golden-yellow.	Lemon-yellow.	Dull brown.

Quercimeritrin, $C_{21}H_{20}O_{12}$, melting-point 247—249°, is contained in cotton flowers (*Gossypium herbaceum*, Linn.) (Perkin, *ibid.*, 1909, 96, 2183), *loc. cit.*, and in the bark of the *Prunus serotina*, Ehrh. (Finnemore, Pharm. Journ., 1910, (iv.), 31, 604). By digestion with boiling dilute sulphuric acid it is hydrolysed according to the equation $C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$ into quercetin and glucose.

Isoquercitrin, $C_{21}H_{20}O_{12}$, melting-point 217—219°, is also contained in cotton flowers, and when hydrolysed by acid gives quercetin and glucose, $C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$.

Incarnatrin, $C_{21}H_{20}O_{12}$, $3H_2O$, is present in the "carnation or crimson" clover, *Trifolium incarnatum*, Linn. (Rogerson, Chem. Soc. Trans., 1910, 97, 1008), and forms yellow prismatic needles, melting-point 242—245°. It is hydrolysed by acid according to the following equation, $C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$, into quercetin and a sugar, the osazone of which melts at 203—205°. It is not identical with quercimeritrin.

Red clover flowers (*Trifolium pratense*, Linn.) also contain a glucoside of quercetin, which crystallises in yellow needles, melting-point 235°, but as yet has not been completely examined (Power and Salway, *ibid.*, 1910, 97, 244).

Other Sources of Quercetin.

See ONION SKINS, PERSIAN BERRIES, SOPHORA JAPONICA, PODOPHYLLUM EMODI, WHITE CLOVER (*Trifolium repens*), CUTCH (*Acacia catechu* and *Uncaria gambier*), and SUMACH, *Osyris compressa*, *Osyris abysinnica*, *Ailanthus glandulosa*, *Rhus rhodanthema*, *Arto-staphylos uva ursi*. Quercetin has also been shown to exist probably as glucoside in tea leaves (Hlasiwetz and Malin, Jahres., 1867, 732); in the flowers of the horse-chestnut (Rochleder, *ibid.*, 1859, 523); in the bark of the apple-tree (Rochleder, *ibid.*, 1867, 731); in *Craetagus oxycantha* (may blossom); and yellow wallflowers, *Cheiranthus chieri* (Perkin and Hummel, Chem. Soc. Trans., 1896, 69, 1568); *Rumex obtusifolius* (seeds), (Perkin, *ibid.*, 1897, 71, 1199); *Delphinium zalil* (Asbarg), (Perkin and Pilgrin, *ibid.*, 1898, 73, 381); *Prunus spinosa* (flowers), (Perkin and Phipps, *ibid.*, 1904, 85, 56), *Thespasia lampas* (Perkin, *ibid.*, 1909, 95, 1859), the flowers of the *Poinciana regia* (Bengal), *Woodfordia floribunda*, and the common fuschia, *F. macrostema globosa* (Perkin and Shulman, Chem. Soc. Proc., 1914, 30, 177).

THUYA OCCIDENTALIS.

Thuya occidentalis (Linn.).—In 1858 Rochleder and Kawalier (Wien. akad. Ber., 29, 10) isolated from the green portions of the

Thuya (*Thuja*) *occidentalis* a glucoside *Thujin*, which, when hydrolysed, gave a yellow colouring matter *thujetin*.

Thujin, $C_{20}H_{22}O_{12}$.—The plant was extracted with alcohol, the extract when cold filtered from wax, and evaporated to a small bulk. The residue was diluted with water, a few drops of lead acetate solution added, the precipitated impurities removed, and the clear brown filtrate treated with lead acetate. The yellow lead compound was collected, extracted with dilute acetic acid, and basic lead acetate now added to the solution. The bright yellow precipitate was suspended in water, decomposed with sulphuretted hydrogen, the lead sulphide removed, the filtrate treated with carbon dioxide in order to free it from sulphuretted hydrogen and evaporated *in vacuo* over sulphuric acid. Crystals gradually separated, and these were crystallised repeatedly from dilute alcohol until when treated with ammonia a green coloration was no longer produced.

Thujin is described by these authors as citron yellow microscopic prisms sparingly soluble in cold water. The alcoholic solution becomes yellow on treatment with alkalis, whereas with ferric chloride a dark green coloration is produced. When thujin is digested in alcoholic solution with dilute hydrochloric or sulphuric acid it is hydrolysed with formation of glucose and *thujigenin*, apparently an intermediate product, which readily takes up a molecule of water, with formation of thujetin—

$$C_{20}H_{22}O_{12} + H_2O = \underset{\text{Thujigenin.}}{C_{14}H_{12}O_7} + C_6H_{12}O_6$$

$$\underset{\text{Thujigenin.}}{C_{14}H_{12}O_7} + H_2O = \underset{\text{Thujetin.}}{C_{14}H_{14}O_8}$$

Thujetin, $C_{14}H_{14}O_8$, forms yellow crystals, and is characterised by the fact that its alcoholic solution is coloured blue-green with ammonia, and green coloured by potassium hydroxide solution.

With lead acetate it gives a deep red precipitate. When thujetin is digested with boiling baryta water it is converted into *thujetinic acid*, $C_{28}H_{22}O_{13}$, which consists of yellow microscopic needles, sparingly soluble in water, readily soluble in alcohol.

Thujigenin, $C_{14}H_{12}O_7$, crystallises in fine yellow needles, soluble in alcoholic ammonia, with a blue-green coloration.

The quantity of thujin which is present in the plant is very small; thus, from 240 lbs. Rochleder and Kawalier were successful in isolating a few grams only.

Perkin (Chem. Soc. Trans., 1914, 105, 1408), who re-examined this subject and employed methods almost identical with those of Rochleder and Kawalier, found that the glucoside corresponding to

thujin possessed the formula $C_{21}H_{20}O_{11}$, melted at 183—185°, and when hydrolysed gave rhamnose and quercetin and was identical with the *quercitrin* of quercitron bark. The plant also contained a small amount of quercetin, and this also, prepared by the hydrolysis of the glucoside which evidently corresponds to the thujetin of Rochleder and Kawalier, dissolved in alkaline solutions with a pale green tint, but failed to give the blue-green coloration with ammonia described by these authors. During a preliminary investigation of this plant (Chem. Soc. Trans., 1899, 75, 829), the sample then examined gave a trace of yellow colouring matter soluble in alkalis with a strong green coloration, the acetyl compound of which after frequent recrystallisation melted at 205—206°. It thus seems probable that the thujin of Rochleder and Kawalier consisted of quercitrin contaminated with a second glucoside, possibly that of myricetin. The quantity of this latter present in the plant may possibly vary according to its environment or with the season of the year.

SOPHORA JAPONICA.

Sophora japonica (Linn.).—This is a large and beautiful tree, not unlike an acacia, belonging to the *Leguminosæ*, which grows abundantly throughout China.

The undeveloped flower-buds constitute an important yellow dyestuff employed by the Chinese for colouring the silken vestments of the mandarins. For this purpose the buds are collected and dried rapidly, either in the sun or by artificial means, usually with the addition of a little chalk. The method of dyeing consists in simply boiling for one to one and a half hours in a decoction of the flower-buds silk which has been previously mordanted by steeping overnight in a decoction of alum. Less frequently it is employed in the dyeing of cotton and wool. Its price appears to be about 30s. a cwt.

This dyestuff has been studied by many chemists, especially by Schunck (Chem. Soc. Trans., 1888, 53, 262; 1895, 67, 30), who has proved that the glucoside which it contains, formerly called sophorin (Förster, Ber., 1882, 15, 214), is in reality identical with rutin, the quercetin glucoside first isolated from rue (*Ruta graveolens*, Linn.) by Weiss (Chem. Zentr., 1842, 903). (Cf. also Stein, J. pr. Chem., (i.), 58, 399; 85, 351; 88, 280; Schunck, Manchester Memoirs, 1858, 2 Ser., 15, 122.) The glucoside is readily isolated by extracting the flower buds with boiling water. The liquid on cooling deposits crystals of rutin, which can be purified by recrystallisation from water or dilute alcohol.

When applied to wool the *Sophora japonica* buds give colours

somewhat like those obtained with quercitron bark, viz. a dull orange with chromium, a yellow of moderate brilliancy with aluminium, a bright yellow with tin, and a dark olive with iron. In dyeing power it seems to be equal if not slightly superior to quercitron bark, and is to be regarded as an excellent natural dyestuff, quite equal to those of similar character in general use (Hummel and Perkin, J. Soc. Chem. Ind., 1895, 458).

Onion Skins (Allium cepa).

The outer dry skins of the bulb of the onion, ***Allium cepa*** (Linn.), were formerly employed for dyeing purposes. According to Leuchs (Farben und Färbekunde, 1825, 1, 434), "the outer skins of onion bulbs which are of a brownish-orange colour have long been used in Germany for dyeing Easter eggs yellow, and in conjunction with alum for dyeing woollen, linen, and cotton materials. The colour is fast and particularly brilliant. From Kurrer's observations onion skins are very suitable for dyeing cotton, on which they give a cinnamon-brown with acetate of alumina, a fawn with alumina and iron, a grey with iron salts, and a variety of shades with other additions."

The colouring matter was extracted by boiling the skins with distilled water for one hour, and the yellow extract on keeping gradually deposited the impure dye as a pale olive precipitate. The average yield was 1·3 per cent. This was extracted with alcohol, the concentrated extract treated with ether and the ethereal solution washed, until a tarry precipitate no longer separated. On extracting the ethereal solution with dilute alkali the whole of the colouring matter was removed, and on neutralising the alkaline liquid a yellow precipitate was thrown down, which was purified by crystallisation from dilute alcohol. The acetyl compound melted at 190—191°, and there could be no doubt as to the identity of this colouring matter with *quercetin* (Perkin and Hummel, Chem. Soc. Trans., 1896, 69, 1295). Attempts to isolate a quercetin glucoside from onion skins have hitherto failed, and it seems that such a compound is absent at least in the outer dry material.

Heather or Calluna vulgaris.

In former times the common heath or heather, until recently named *Erica vulgaris*, was used as a dyestuff for producing a yellow colour on woollen goods (Crookes, "Dyeing and Calico Printing," 1874, p. 511). Although now almost superseded it was until recently employed in the home industries of outlying districts, such as the Highlands of Scotland. Bancroft ("Philosophy of Permanent

Colours," 1813, 2, 108) states that all five species of the *erica* or heather found in Great Britain are, he believes, capable of giving yellows much like those obtained from dyer's brown. According, however, to the experiments of the late J. J. Hummel the *E. tetralix* (bell heather) and *E. cinerea* contain only traces of yellow colouring matter. Leuchs (Farben u. Färbekunde, 2, 320) refers to the tanning property of heather, and notes that the effect resembles in character that given by oak bark. H. R. Procter found it to contain 6·4 per cent. of tannin. The colouring matter was isolated by Perkin and Newbury (Chem. Soc. Trans., 1899, 75, 837) from an aqueous extract of the green portion of the plant, in which it appears only to reside, by precipitation with lead acetate in the usual manner. It proved to be identical with the *quercetin* of quercitron bark. The dyeing properties of heather, though distinctly weaker, are so similar in character to those given by quercitron bark as to require no special description. Experiment showed that 36 parts of the heather were necessary to obtain as good a result as that given by 10 parts of quercitron bark.

THESPASIA MACROPHYLLA.

Thespasia macrophylla, Blume (*T. lampas*, Dabz.).—This is a small bush common to the tropical jungles of India, Burma, and Ceylon. In Watt's "Dictionary of the Economic Products of India" there is no mention of the use of this plant as a dyestuff, but, on the other hand, the capsules and flowers of the allied *T. populnea* (Soland) are stated to give a yellow dye.

According to Perkin (Chem. Soc. Trans., 1909, 95, 1859) the flowers of the *T. macrophylla* yield *quercetin* and some quantity of *protocatechuic acid*.

With mordanted woollen cloth the flowers produce fairly good shades, but are in no way superior to the better-known Indian natural yellow dyestuffs.

EUCALYPTUS MACRORHYNCHA.

Eucalyptus macrorhyncha (F. v. M.), a fair-sized tree, is the "red stringy bark" of New South Wales, and the ordinary stringy bark tree of Victoria (Smith, Chem. Soc. Trans., 1898, 73, 697).

The leaves yield under favourable conditions a very large amount (10 per cent.) of a crystalline glucoside termed by Smith *myrticolorin*, which can be isolated in the crude condition by mere extraction with boiling water. The solution on cooling became semi-solid owing to the separation of crystals, and these can be purified by extraction

with ether to remove chlorophyll and crystallisation first from alcohol and subsequently from water. It formed pale yellow needles, gave on hydrolysis quercetin and glucose, and at first appeared to be a new glucoside of quercetin. Though very similar to rutin its identity with this glucoside was unsuspected in that rutin by hydrolysis was presumed at that time to give quercetin and 2 molecules of rhamnose (Schunck, *ibid.*, 1888, 53, 264). Schmidt in 1908 (Arch. Pharm., 246, 214), however, pointed out that rutin in this manner yields not only rhamnose but glucose, and the probability that myrticolorin—as also viola quercitrin and osyritrin (*loc. cit.*)—were identical with rutin was subsequently confirmed by Perkin (*ibid.*, 1910, 97, 1776).

Podophyllum emodi.

P. emodi is a small herbaceous plant growing abundantly in Northern India. The root, or rather the rhizome, is employed medicinally in India as a powerful purgative, just, indeed, as the allied *P. peltatum* is used in Europe and America.

An examination of this root by Dunstan and Henry (Chem. Soc. Trans., 1898, 73, 209) has shown that in addition to *podophyllotoxin*, the active constituent, a considerable quantity of *quercetin* is present. According to Hummel this material in dyeing property compares favourably with quercitron bark, and should prove commercially valuable as a dyestuff at least to the native dyer.

Clover Flowers.

It has long been known that clover flowers dye a yellow colour on aluminium mordanted fabrics, and in the past they have been employed to a minor extent for dyeing purposes. Three varieties have been chemically examined, viz. those derived from the *Trifolium pratense*, the *T. incarnatum*, and the *T. repens*.

Trifolium pratense.—The flowers known as the "common red clover," according to Power and Salway (Chem. Soc. Trans., 1910, 97, 231), contain in addition to *isorhamnetin* (quercetin monomethyl ether) and a *glucoside of quercetin*, melting-point 235°, numerous other phenolic substances, which, judging by their chemical properties, appear to be closely allied to the colouring matters of the flavone group. These are described below.

Pratol, $C_{15}H_8O_2(OH).OCH_3$, colourless needles, melting-point 253°, readily soluble in hot aqueous sodium carbonate and sodium hydroxide with a pale yellow coloration, yields the *acetyl* compound, $C_{15}H_8O_2(OC_2H_3O).OCH_3$, and is probably a *hydroxymethoxyflavone*.

A new *yellow compound*, $C_{16}H_{10}O_7$, thin yellow plates, melting-

point about 280°, is soluble in alkalis with a yellow colour, and its solution in sulphuric acid exhibits a brilliant green fluorescence. It contains a methoxy group and gives an acetyl compound,

$$C_{16}H_6O_7(C_2H_3O)_4,$$

melting-point 145—147°.

Pratensol, $C_{17}H_9O_2(OH)_3$, is very readily soluble in alcohol, dissolves in alkali carbonates yielding yellow solutions, and its alcoholic solution gives with ferric chloride a greenish-black coloration. *Triacetylpratensol*, $C_{17}H_9O_5(C_2H_3O)_3$, colourless slender needles, melts at 189°.

A new *phenolic substance*, $C_{15}H_7O_3(OH)_3$, colourless needles, melting-point 225°, is soluble in alkali hydroxides, and gives with alcoholic ferric chloride a dark green coloration. The *acetyl* derivative, silky needles, has melting-point 209°.

The glucoside *trifolin*, $C_{22}H_{22}O_{11}$, H_2O, pale yellow needles, melts and decomposes at about 260°. It is soluble in alkalis with an intense yellow coloration, and dissolves in sulphuric acid, forming a yellow solution, which rapidly develops a brilliant green fluorescence. When hydrolysed it yields rhamnose and *trifolitin*, $C_{16}H_{10}O_6$, melting-point about 275°, readily soluble in alcohol,

$$C_{22}H_{22}O_{11} = C_{16}H_{10}O_6 + C_6H_{12}O_5$$

Alkalis dissolve trifolitin with an intense yellow colour, alcoholic ferric chloride gives a dark green coloration, and alcoholic lead acetate an orange-yellow lead salt. It contains no methoxy group, and is unaltered when heated for several hours with 30 per cent. aqueous potassium hydroxide. It does not appear to belong to the flavone group, and differs from the flavone compounds by the fact that it does not give an oxonium salt with sulphuric acid, and only with difficulty a potassium compound by means of alcoholic potassium acetate. It may possibly consist of a tetrahydroxyphenylnaphthoquinone. The acetyl compound when rapidly heated melted at 116°, re-solidified at a higher temperature, and finally melted at 182°.*

The glucoside *isotrifolin*, $C_{22}H_{22}O_{11}$, isomeric with trifolin, consists of pale yellow needles, melting-point about 250°, and when hydrolysed yields similarly to the latter trifolitin, $C_{16}H_{10}O_6$, melting-point 275°. Though in general behaviour it is very similar to *trifolin*, it is much more soluble in alcohol, and does not appear to be identical with this glucoside.

In addition to these compounds the flowers contain *salicylic acid*, *coumaric acid*, *myricyl alcohol*, $C_{31}H_{63}OH$, *heptacosane*, $C_{27}H_{56}$,

* Both in its melting-point and that of its acetyl derivative there is a marked resemblance between trifolitin and kaempferol.

hentriacontane, $C_{31}H_{64}$, *sitosterol*, $C_{27}H_{46}O$, *trifolianol*, $C_{21}H_{24}O_2(OH)_2$, *palmitic*, *stearic*, *linolic*, *oleic*, *linolenic*, and *isolinolenic acids*.

TRIFOLIUM INCARNATUM.

A considerable difference is exhibited between the constituents of the "carnation or crimson clover flowers" and those of the *T. pratense* or "common red clover".

According to Rogerson (Chem. Soc. Trans., 1910, 97, 1006) these flowers contain *pratol*, $C_{15}H_8O_2(OH)(OCH_3)$, free *quercetin*, and a *glucoside of quercetin*, $C_{21}H_{20}O_{12}$, $3H_2O$, to which the name *incarnatrin* is applied. This latter crystallises in yellow prismatic needles, melting-point 242—245°, dissolves in sulphuric acid with formation of a green fluorescent solution, and when hydrolysed yields quercetin and glucose according to the equation

$$C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$$

Incarnatrin is not identical with the quercimeritrin of Perkin (Chem. Soc. Trans., 1909, 95, 2181).

In addition to these substances the flowers yield *furfuraldehyde*, *benzoic* and *salicylic acids*, a trace of *p-coumaric acid*, *incarnatyl alcohol*, $C_{24}H_{69}OH$, *hentriacontane*, $C_{31}H_{64}$, a *phytosterol*, $C_{27}H_{46}O$, and *palmitic*, *stearic*, *oleic*, *linolenic*, and *isolinolenic acids*.

TRIFOLIUM REPENS.

The flowers of the white clover, *T. repens*, according to Perkin and Phipps (Chem. Soc. Trans., 1904, 85, 58), owe their tinctorial property to quercetin which is present as glucoside.

PRUNUS EMARGINATA (?).

The bark of a spurious substitute for that of the *Prunus serotina*, probably *P. emarginata*, has been shown by Finnemore (Pharm. Journ., 1910, (iv.), 31, 604) to contain in addition to quercimeritrin (Perkin, Chem. Soc. Trans., 1909, 95, 243) a glucoside *prunitrin*, $C_{22}H_{24}O_{11}$, $4H_2O$, fine needles, which when hydrolysed yields *prunetin* and glucose.

Prunetin, $C_{15}H_9O_4 . OCH_3$, colourless needles, melting-point 242°, dissolves in alkalis with a slight yellow colour, and is sparingly soluble in all the usual solvents. *Monacetylprunetin*, $C_{16}H_{11}O_5(C_2H_3O)$, pale yellow needles, melting-point 190°; *diacetylprunetin*,

$$C_{16}H_{10}O_5(C_2H_3O)_2,$$

melting-point 224—226°; *benzoylprunetin*, $C_{16}H_{10}O_5(C_7H_5O)_2$, needles, melting-point 215°; *dimethylprunetin*, $C_{15}H_8O_3(OCH_3)_2$, needles, melting-point 145°; and *acetyldimethylprunetin*, $C_{15}H_7O_3(OCH_3)_2C_2H_3O$, have been prepared.

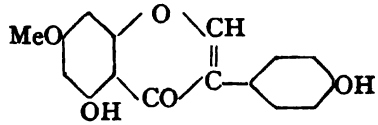
Fused with caustic potash at 250°, prunetin gives *phloroglucinol* and *p-hydroxyphenylacetic acid*.

Prunetol, $C_{15}H_{10}O_5$, colourless needles, melting-point 290°, is formed by the demethylation of prunetin with hydriodic acid, and yields *acetylprunetol*, $C_{15}H_7O_5(C_2H_3O)_3$, and *prunetol sulphate*,

$$C_{15}H_{10}O_5 . H_2SO_4,$$

yellow needles. On methylation with methyl iodide *prunetol dimethyl ether*, identical with prunetin monomethyl ether, and a sparingly soluble methyl ether, the acetyl derivative of which melts at about 186°, are produced (Finnemore, Chem. Soc. Trans., 1910, 98, 1102).

It is considered by this author that prunetin is closely related to scutellarein (Molisch and Goldschmiedt, *loc. cit.*) and may have the constitution—



Persian Berries.

Persian berries are the seed-bearing fruit of various species of *Rhamnus*, growing wild or cultivated in France, Spain, Italy, the Levant, and Persia. The Persian berry proper is obtained from *R. amygdalinus*, *R. oleoides*, and *R. saxatilis*, and is imported from Smyrna and Aleppo. Its size is about that of a pea, colour yellowish-green, surface much shrivelled, hard, and divisible along well-marked depressions forming a cross, into four parts, each containing a triangular seed; its taste is intensely bitter.

Avignon or French berries, the product of *R. infectorius* (Linn.) and *R. alaternus* (Linn.), are smaller in size than the foregoing and contain only two seeds.

Spanish, Italian, and Hungarian berries are respectively the products of *R. saxatilis*, *R. infectorius* (Linn.), and *R. cathartica* (Linn.). These are similar in quality to the Avignon berries. Other qualities come from the Morea, Wallachia, and Bessarabia.

All of these botanical varieties do not contain entirely the same constituents, but, on the other hand, there is every reason to suppose that the colouring constituents of those to which the term Persian berry proper is applied are identical in each case.

Gelatly (Edinburgh New Phil. Jour., 7, 252) was the first to isolate from Persian berries (*R. tinctoria*, Wald. et Kit.) the glucoside *xanthorhamnin*, $C_{45}H_{56}O_{28}$, which on hydrolysis with acid gave a

sugar and a colouring matter *rhamnetin*. Hlasiwetz (Annalen, 112, 107) considered that xanthorhamnin was identical with quercitrin, and rhamnetin with quercetin, but Schützenberger and Bertèche (Bull. Soc. Ind. Mulhouse, 35, 456) denied this, and assigned to rhamnetin the formula $C_{12}H_{10}O_5$. Xanthorhamnin, which Schützenberger (Jahres., 1868, 774) termed *α-rhamnegin* was considered to possess the formula $C_{24}H_{32}O_{14}$. The presence of a second glucoside, *β-rhamnegin*, was also detected by this chemist, and from this by hydrolysis *β-rhamnetin* was derived. Liebermann and Hörmann (Annalen, 196, 313) also investigated Persian berries, devised a method for the preparation of xanthorhamnin and rhamnetin, and prepared various derivatives of the latter.

It is now known that Persian berries contain the glucosides of three colouring matters, namely rhamnetin, rhamnazin, and quercetin (Herzig, Monatsh., 6, 889; 9, 549; 12, 175; Perkin and Geldard, Chem. Soc. Trans., 1895, 67, 500).

To isolate these substances Persian berries are extracted with boiling water, the solution treated with a small quantity of sulphuric acid, and digested while boiling for one hour. The glucosides are thus hydrolysed and the crude colouring matters separate in the form of a greenish-yellow precipitate.

The product is extracted with boiling alcohol, which dissolves principally the *quercetin*, this being the most soluble of the three colouring matters. The residue now contains rhamnetin and rhamnazin, and the latter is removed from the former by two or three extractions with boiling acetic acid.

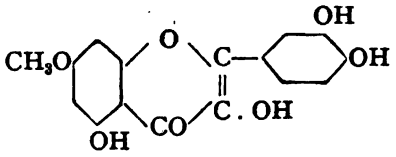
Rhamnetin, $C_{16}H_{12}O_7$, crystallises in yellow needles very sparingly soluble in acetic acid and alcohol. It dissolves in alkaline solutions with a pale yellow colour, and gives with alcoholic lead acetate an orange-red precipitate. When acetylated it forms *tetra-acetylrhamnetin*, $C_{16}H_8O_7(C_2H_3O)_4$ (Liebermann and Hörmann), colourless needles, melting-point 183—185°, and on bromination *dibromrhamnetin* is produced.

Rhamnetin sulphate, $C_{16}H_{12}O_7 . H_2SO_4$ (Perkin and Pate, Chem. Soc. Trans., 1895, 67, 650), orange-red needles, and *monopotassium rhamnetin*, $C_{16}H_{11}O_7K$ (Perkin and Wilson, *ibid.*, 1903, 83, 136), orange-yellow needles, have been prepared.

Rhamnetin is in reality a *quercetinmonomethyl ether* (Herzig, *loc. cit.*), for on digestion with hydriodic acid it is converted into *quercetin*, and when methylated with methyl iodide *quercetintetramethyl ether* is produced.

By the action of boiling potassium hydroxide solution, of boiling

alcoholic potash, or by aspirating air through its alkaline solution, rhamnetin gives *protocatechuic acid*, and a syrupy phloroglucinol derivative. The latter, identified by means of its diazobenzene compound, consists of *phloroglucinol monomethyl ether* (Perkin and Allison, Chem. Soc. Trans., 1902, 81, 470), and consequently the constitution of rhamnetin is to be expressed as follows:—



Rhamnetin is a strong dyestuff, and gives on mordanted woollen cloth shades which are practically identical with those produced by quercetin:—

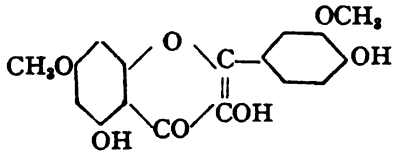
Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Red-brown.	Brown-orange.	Bright orange.	Deep olive.

(Perkin and Wilkinson, *ibid.*, 1902, 81, 590).

Rhamnazin, $C_{17}H_{14}O_7$ (P. and G.), yellow needles, melting-point 214—215°, is moderately soluble in boiling toluene, a property which distinguishes it from both rhamnetin and quercetin. It dissolves in alkaline liquids to form orange-yellow solutions, and with alcoholic ferric chloride gives an olive-green coloration.

Acetylrhamnazin, $C_{17}H_{11}O_7(C_2H_3O)_3$, colourless needles, *benzoylrhamnazin*, $C_{17}H_{11}O_7(C_7H_5O)_3$, colourless needles, melting-point 204—205°, and *dibromrhamnazin*, $C_{17}H_{12}Br_2O_7$, yellow needles, have been prepared.

Rhamnazin is a *quercetin dimethyl ether*. Digested with boiling hydriodic acid, it is converted into quercetin, and by methylation in the ordinary manner gives quercetin tetramethyl ether. Boiling alcoholic potash hydrolyses rhamnazin with formation of *vanillic acid* and *phloroglucinol monomethyl ether* (Perkin and Allison, *loc. cit.*). It accordingly possesses the constitution—



Rhamnazin does not readily dye mordanted calico, but on mordanted wool gives shades resembling those which are produced by kaempferol—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Golden-yellow.	Orange-yellow.	Lemon-yellow.	Olive-brown.

Only a small amount of this colouring matter is present in Persian berries.

Xanthorhamnin, $C_{24}H_{42}O_{20}$, is readily prepared by extracting powdered Persian berries with three times their weight of boiling 85 per cent. alcohol. On standing the dark brown filtered extract deposits a large quantity of the impure glucoside as a brown resinous mass. From the supernatant liquid on standing a purer xanthorhamnin separates in the form of a pale yellow cauliflower-like precipitate, and in such quantity as to congeal the whole liquid to a stiff paste. This is collected, repeatedly crystallised from alcohol, and finally from alcohol containing a little water and ether (Liebermann and Hörmann, *loc. cit.*).

Xanthorhamnin consists of pale yellow needles readily soluble in water and hot alcohol, soluble in alkaline solutions with a yellow colour. With basic lead acetate it gives an orange precipitate. According to the work of Liebermann and Hörmann, xanthorhamnin, when hydrolysed with acid, gives *rhamnetin* and *rhamnose*,

$$C_{48}H_{66}O_{29} + 5H_2O = 4C_6H_{14}O_6 + 2C_{12}H_{10}O_5$$

More recently, however, xanthorhamnin has been shown to possess the formula $C_{24}H_{42}O_{20}$, and that by means of its specific ferment *rhamninase*, contained by Persian berries, it is hydrolysed with formation of rhamnetin and a complex sugar *rhamninose*, $C_{18}H_{32}O_{14}$,

$$C_{24}H_{42}O_{20} + H_2O = C_{16}H_{12}O_7 + C_{18}H_{32}O_{14}$$

When rhamninose is digested with boiling dilute acids, it is converted into 2 molecules of *rhamnose*, and 1 molecule of *galactose* (C. and G. Tanret, Comptes rend., 1899, 129, 725),

$$C_{18}H_{32}O_{14} + 4H_2O = C_6H_{12}O_6 + 2C_6H_{14}O_6$$

No glucosides of rhamnazin or quercetin have been isolated as yet from Persian berries.

The action of the ferment rhamninase is readily demonstrated. If crushed Persian berries, contained in a muslin bag, are suspended in water heated to 40°, a yellow solution containing the glucosides is produced; this quickly becomes opaque and a heavy precipitate of the mixed colouring matters eventually separates. To within recent years this reaction was carried out on a commercial scale, and the product was placed on the market under the name of "rhamnétine". This reaction can be employed to distinguish between the dyeing properties of the glucosides contained in

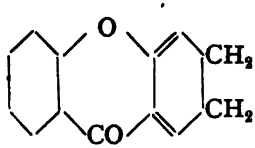
the berries, and the free colouring matters produced by their hydrolysis. Thus if Persian berries be added to a cold dye-bath, and this is slowly heated to boiling, the glucosides are hydrolysed by the ferment; but if, on the other hand, the berries be at once plunged into boiling water, the ferment is killed and a solution of the glucosides is obtained. In the former case wool mordanted with tin gives an orange-red shade, whereas in the latter a pure yellow colour is produced.

Beyond the ordinary extract of Persian berries which is prepared in large quantity by extracting the berries with boiling water, and evaporating the solution under reduced pressure, no special commercial preparations are manufactured at the present time.

Dyeing Properties.—In wool dyeing Persian berries are little employed on account of their cost; moreover, they possess no special advantage over quercitron bark and old fustic. Persian berries, as a rule, give redder shades than quercitron bark, a fact which is to be explained as due to the hydrolysis of its glucosides by the ferment. The quercitrin of quercitron bark is not accompanied by such a specific ferment, and consequently the shades given by this dyestuff are of a yellower character. With tin mordant Persian berries give bright yellows and oranges, which are only fairly fast to light; but according to Hummel, the yellowish-olive produced with copper mordant is extremely fast, and is darkened rather than otherwise by exposure. Persian berries are still used to a considerable extent in calico-printing for the formation of yellow, orange, and green shades.

Rhamnus catharticus.

The *Rhamnus catharticus* or Purging Buckthorn, indigenous to Great Britain, is a stiff many-branched shrub growing from five to ten feet high, the fruit of which consists of small berries, resembling when dry black pepper-corns. Formerly it was in great demand as a medicine, but has now fallen into disrepute. The juice of the berries admixed with lime and evaporated to dryness constitutes the pigment known as "sap" or "bladder green". According to Tschirch and Polacco (Arch. Pharm., 1900, 238, 459) the yellow tinctorial constituents yielded by the berries of this plant are quite distinct from those given by the berries of the various species of *Rhamnus* which constitute the Persian berry proper. Thus in addition to rhamno-emodine they isolated four yellow crystalline substances, rhamnocitrin, β-rhamnocitrin, rhamnochrysin, and rhamnolutin. Rhamnocitrin was considered to consist of the trihydroxy derivative of a dihydroxanthone—



rhamnolutin of a tetrahydroxyflavone isomeric with luteolin and fisetin, and rhamnochrysin an oxidation product of rhamnocitrin, whereas β-rhamnocitrin was distinct from rhamnetin and indeed contains no methoxy groups.

Valiaschko and Krasowski (J. Russ. Phys. Chem. Soc., 1908, 40, 1502) and Krasowski (*ibid.*, 1510) criticised this paper of Tschirch and Polacco, and could not isolate the compounds described by these latter authors. On the other hand, quercetin, rhamnetin, and xanthorhamnin, the glucoside of rhamnetin, were found to exist in these berries, and it seemed likely that the rhamnolutin of Tschirch and Polacco was rhamnetin and their rhamnochrysin a mixture of quercetin and emodine.

Oesch and Perkin (Chem. Soc. Trans., 1914, 105, 2350) also isolated *rhamnetin* from these berries, together with a small amount of quercetin, and considered that the former represents the β-rhamnocitrin of Tschirch and Polacco. The main colouring matter present, however, is *kaempferol*, $C_{15}H_{10}O_6$, the trihydroxyflavonol which can be obtained from the flowers of the *Delphinium zalil* and *D. consolida*, and this is to be regarded as the so-called " rhamnolutin ".

A fourth compound, evidently the rhamnocitrin of these latter authors, possessed the formula $C_{16}H_{12}O_6$, rather than $C_{15}H_{10}O_5$ which they assigned to it. This crystallised in yellow leaflets, melting-point 221—222°, and its acetyl derivative at 200—201°, and these melting-points are practically the same as those given by Tschirch and Polacco. It contains one methoxy group, by the action of hydriodic acid yields *kaempferol*, and is evidently a *kaempferol monomethyl ether*. It bears considerable resemblance to kaempferide, a monomethyl ether of kaempferol present in Galanga root, *Alpinia officinarum* (Jahresber., 1881, 14, 2385), which, however, melts at 227—229°, and its acetyl derivative at 193—195°, and though there is thus strong probability that the two compounds are not identical, Oesch and Perkin suggest that further work on this point is desirable.

ASBARG.

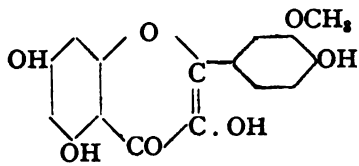
Asbarg consists of the dried flowers and flowering stems of the *Delphinium zalil*, which is found in great quantity in Afghanistan. The dyestuff is collected and taken to Multan and other Punjab

towns, from which it is conveyed all over India. It is much used in silk dyeing for the production of a sulphur-yellow colour known as "gandkaki," and, together with *Datisca cannabina*, to obtain a similar shade on alum-mordanted silk; it is also used in calico-printing. The flowers, which are bitter, are likewise employed medicinally as a febrifuge.

The colouring matters of asbarg are present entirely as glucosides, and are best isolated in the crude condition by digesting the boiling aqueous extract with a little sulphuric acid (Perkin and Pilgrim, Chem. Soc. Trans., 1898, 268). A brownish-yellow powder thus separates, which contains three substances: *isorhamnetin*, *quercetin*, and *kaempferol*.

Iso*rhamnetin*, $C_{16}H_{12}O_7$, the sparingly soluble constituent, forms yellow needles, resembling rhamnetin in appearance. With lead acetate in alcoholic solution, an orange-red precipitate is formed, whilst ferric chloride gives a greenish-black coloration. Fused with alkali, *phloroglucinol* and *protocatechuic acid* are produced, and when air is aspirated through its alkaline solution, *phloroglucinol* and *vanillic acid* are obtained.

With acetic anhydride *iso*rhamnetin gives a *tetra-acetyl* derivative, $C_{16}H_8O_7(C_2H_3O)_4$, colourless needles, melting-point 195—196°; and with methyl iodide a *trimethyl ether*, which is identical with *quercetin tetramethyl ether*. As, moreover, by the action of hydriodic acid *iso*rhamnetin yields quercetin, its constitution can only be represented as follows:—



The dyeing properties of *iso*rhamnetin are similar in character to those given by kaempferol. *iso*Rhamnetin is also present in yellow wallflowers (*Cheiranthus cheiri*) (Perkin and Hummel), and in red clover flowers, *Trifolium pratense* (Power and Salway, Chem. Soc. Trans., 1910, 97, 245). A description of the more soluble colouring matters quercetin (*quercitron bark*) and kaempferol (*Delphinium consolida*) is given elsewhere.

In dyeing properties asbarg closely resembles quercitron bark, but yields with aluminium mordant a purer or less orange-yellow. It is, however, a much weaker dyestuff, having but 35 per cent. the dyeing power of quercitron bark. The colouring matter of the flowers,

apart from the flowering-stalks, is present to the extent of 3·47 per cent.

The stems and flowers of the *D. saniculæfolium* give shades analogous to, though somewhat weaker than, those yielded by the *D. salil.*

Yellow Wallflower—Cheiranthus cheiri.

The purplish-brown petals of the common garden wallflower are comparatively rich in colouring matter, though the shade given by these on alumina mordant possesses a greenish-olive-yellow tint, and is of a less pure character than that given by the variety known as "Cloth of Gold". A boiling aqueous extract of these latter flowers on treatment with sulphuric acid gradually deposits a yellow precipitate, and this is most readily purified by pouring the concentrated alcoholic solution into much ether. The main impurity is thus precipitated, whereas the colouring matter remains dissolved in the ether. By fractional crystallisation from alcohol two colouring matters can be isolated from this product, (*a*) sparingly soluble which consists of *isorhamnetin* (quercetin monomethyl ether) and (*b*) *quercetin*. The existence of isorhamnetin was first demonstrated by an examination of these flowers (Perkin and Hummel, Chem. Soc. Trans., 1896, 69, 1566).

Old Fustic.

Old fustic is the wood of a tree known as the *Chlorophora tinctoria* (Gaudich), previously called *Morus tinctoria* (Linn.), which occurs wild in different tropical regions. The tree frequently grows to a height of over 60 feet, is exported in the form of logs, sawn straight at both ends, and usually deprived of the bark. The best qualities of old fustic come from Cuba and the poorer from Jamaica and Brazil. It is at the present time used very largely, and, together with logwood, is the most important of the natural dyestuffs.

The colouring matters of old fustic were first investigated by Chevreul ("Leçons de chimie appliquée à la teinture," ii., 150), who described two substances, one sparingly soluble in water, called *morin*, and a second somewhat more readily soluble. Wagner (J. pr. Chem., (i.), 51, 82) termed the latter *moritannic acid*, and considered that it possessed the same percentage composition as morin. Hlasiwetz and Pfaundler (Annalen, 127, 351), on the other hand, found that the so-called moritannic acid was not an acid, and as moreover its properties were quite distinct from those of morin, they gave it the name "Maclurin".

Morin, $C_{15}H_{10}O_7$, $2H_2O$.—To isolate this colouring matter from old fustic a boiling extract of the rasped wood is treated with a little

acetic acid and then with lead acetate solution. This causes the precipitation of the morin in the form of its yellow lead compound, whereas the main bulk of the maclurin remains in solution. The washed precipitate in the form of a thin cream is run into boiling dilute sulphuric acid, and the hot liquid, after decantation from the lead sulphate, is allowed to stand. Crystals of crude morin are gradually deposited, and a further quantity can be isolated from the acid solution by means of ether. During the preparation of commercial fustic extract, the solution on standing, or the concentrated extract itself, deposits, as a rule, a brownish-yellow powder, which consists principally of a mixture of morin and its calcium salt, and this forms the best source for the preparation of large quantities of the colouring matter. The product is digested with a little boiling dilute hydrochloric acid to decompose the calcium compound, extracted with hot alcohol, and the extract evaporated. Crystals of morin separate on standing, and a further quantity can be isolated by the cautious addition of a little boiling water to the mixture.

Crude morin can be partially purified by crystallisation from dilute alcohol or dilute acetic acid, but the product usually contains a trace of maclurin. To remove the latter the finely powdered substance is treated in the presence of a little boiling acetic acid with fuming hydrobromic acid (or hydrochloric acid), which precipitates the morin as halogen salt, whereas the maclurin remains in solution (Bablich and Perkin, Chem. Soc. Trans., 1896, 69, 792). The crystals are collected, washed with acetic acid, decomposed by water, and the regenerated morin crystallised from dilute alcohol.

Morin crystallises in colourless needles (Bablich and Perkin), readily soluble in boiling alcohol, soluble in alkaline solutions with a yellow colour. Lead acetate solution gives a bright orange-coloured precipitate and ferric chloride an olive-green coloration.

Loewe (Zeitsch. anal. Chem., 14, 112) was the first to assign to morin the formula $C_{15}H_{10}O_7$, and that this was correct was shown by the analysis of its compounds with mineral acids (Perkin and Pate, Chem. Soc. Trans., 1895, 67, 649). The *hydrochloride*, *hydrobromide*, and *hydriodide* are obtained in orange-coloured needles, and possess the formula $C_{15}H_{10}O_7 . HCl$; $C_{15}H_{10}O_7 . HBr$; and $C_{15}H_{10}O_7 . HI$, but the sulphuric acid compound, known as *anhydromorin sulphate*, $C_{15}H_8O_6 . H_2SO_4$, orange-red needles, is of an abnormal character. *Monopotassium morin*, $C_{15}H_9O_7K$, yellow needles, *monosodium morin*, $C_{15}H_9O_7Na$, *magnesium morin*, $(C_{15}H_9O_7)_2Mg$, orange-yellow needles, and *barium morin*, $(C_{15}H_9O_7)_2Ba$, orange crystalline powder, have also been prepared (Perkin, Chem. Soc. Trans., 1899, 75, 437).

When an alcoholic solution of morin is treated with bromine (Benedikt and Hazura, Monatsh., 5, 667; Hlasiwetz and Pfaundler, Jahres., 1864, 557) it is converted into *tetrabrom-morin ethyl ether*,

$$C_{15}H_5Br_4O_7Et, 2H_2O,$$

colourless needles, melting-point 155° (Herzig, Monatsh., 18, 700), and this when digested with stannous chloride and hydrochloric acid gives *tetrabrom-morin*, $C_{15}H_6Br_4O_7$ (Benedikt and Hazura), colourless needles, melting-point 258°. According to Bablich and Perkin, this latter compound is more simply prepared by the direct bromination of morin suspended in acetic acid.

By the action of acetic anhydride on morin according to the usual methods, a colourless amorphous product results, and a crystalline pentacetylmorin has not yet been prepared. Cold acetic anhydride, however, converts the monopotassium salt of the colouring matter into *tetra-acetylmorin*,

$$C_{15}H_6O_7(C_2H_3O)_4,$$

colourless prismatic needles, melting-point 142—145°, but this on further acetylation gives an amorphous compound.

Tetrabromomorin, on the other hand, yields a *penta-acetyl derivative* (Bablich and Perkin), $C_{15}HBr_4O_7(C_2H_3O)_5$, colourless needles, 192—194°, and it was subsequently found by Herzig that tetrabrommorin ethyl ether yields the compound $C_{15}HBr_4O_7Et(C_2H_3O)_4$, melting-point 116—120°.

By fusion with alkali morin gives *phloroglucinol* (Hlasiwetz and Pfaundler) and *resorcinol* (Benedikt and Hazura), whereas in this manner Bablich and Perkin isolated also *β-resorcylic acid*. When methylated with methyl iodide *morin tetramethyl ether*,

$$C_{15}H_6O_3(OCH_3)_4$$

(Bablich and Perkin), yellow needles, melting-point 131—132°, is produced, but is isolated with difficulty, and from this compound with alcoholic potash a yellow potassium salt, readily decomposed by water, is obtained. *Monoacetyltetramethylmorin*,

$$C_{15}H_5O_3(OCH_3)_4C_2H_3O,$$

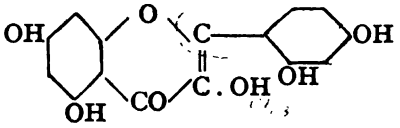
colourless needles, melts at 167°.

Morin tetraethyl ether, $C_{15}H_6O_3(OC_2H_5)_4$ (Perkin and Phipps, Chem. Soc. Trans., 1904, 85, 61), yellow needles, melting-point 126—128°, and *acetylmorin tetraethyl ether*,

$$C_{15}H_5O_3(OC_2H_5)_4C_2H_3O,$$

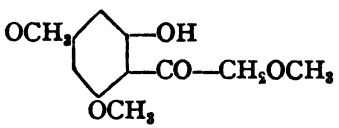
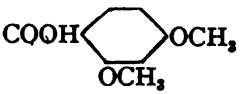
colourless needles, melting-point 121—123°, could only be prepared in small quantity.

When *morin tetramethyl ether* is hydrolysed with alcoholic potash, *β-resorcylic acid dimethyl ether* and *phloroglucinolmonomethyl ether* are produced. Bablich and Perkin assigned to morin the constitution of a *pentahydroxyflavone* (tetrahydroxyflavonol)—



and that this formula correctly represents the substance has been proved by its synthesis (v. Kostanecki, Lampe, and Tambor, Ber., 1906, 39, 625) and also by the investigation of Herzig and Hofmann (Ber., 1909, 42, 155). It has been shown by the latter chemists that when morin is methylated by means of methyl sulphate *morin pentamethyl ether*, $C_{15}H_5O_2(OCH_3)_5$, needles, melting-point 154—157°, can be produced, though for this purpose Perkin and Watson (Chem. Soc. Trans., 1915, 107, 207) prefer the modification of Valiaschko's process (Arch. Pharm., 1904, 242, 242) previously found serviceable for the preparation of quercetin pentamethyl ether by Watson.

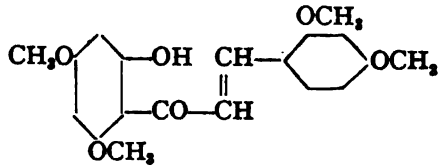
Morin pentamethyl ether is hydrolysed with boiling alcoholic potash into *methoxy fisetol dimethyl ether* (1), and *β-resorcylic acid dimethyl ether* (2) (cf. Quercetin and Fisetin)—

(1)  (2) 

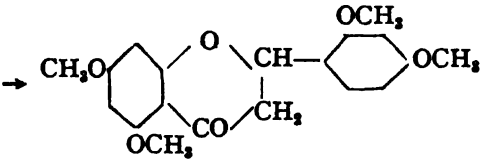
the former being identical with the compound obtained in a similar way from quercetin pentamethyl ether. By nitration it forms *nitromorin pentamethyl ether*, $C_{15}H_4O_2(OMe)_5NO_2$, reddish-brown needles, melting-point 223—225°, and this when reduced with alcoholic hydrochloric acid and tin gives *aminomorin pentamethyl ether*, colourless hexagonal plates, melting-point 204—205°, the *platinichloride*, $(C_{20}H_{21}O_7N)_2H_2PtCl_6$, of which forms stout yellow prisms. Attempts to prepare the hydroxy compound from this amino derivative were unsuccessful. *Aminomorin*, $C_{15}H_4O_2(OH)_5NH_2$, obtained from the nitropentamethyl ether with hydriodic acid is yellowish-brown and dissolves in alkalis to form a brownish-yellow solution. The hydriodide $C_{15}H_4O_2(OH)_5NH_2 . HI, H_2O$ crystallises in square platelets (Perkin and Watson).

v. Kostanecki, Lampe, and Tambor (Ber., 1906, 39, 625) have synthesised morin by reactions similar to those found serviceable in the artificial preparation of fisetin and quercetin (see Young Fustic

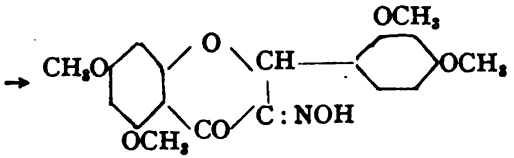
and Quercitron Bark), but in this case the formation of the flavanone did not proceed smoothly and only a small quantity could be prepared. The synthesis is illustrated by the following formulæ:—



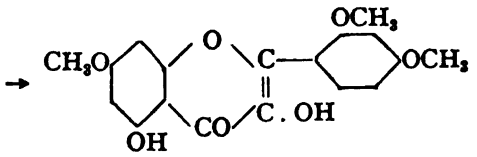
2'-hydroxy-4 : 6 : 2' : 4'-tetramethoxychalkone.



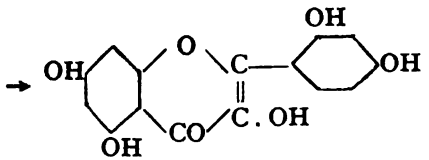
1 : 3 : 2' : 4'-tetramethoxyflavanone.



a-isonitroso-1 : 3 : 2' : 4'-tetramethoxyflavanone.



Morin trimethyl ether.



Morin.

Morin dyes mordanted woollen cloth shades which, though of a slightly stronger character, closely resemble those given by kaempferol.

	Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Morin .	Olive-yellow.	Yellow.	Lemon-yellow.	Deep olive-brown.
Kaempferol	Brown-yellow.	Yellow.	Bright yellow.	Deep olive-brown.

(Perkin and Wilkinson, Chem. Soc. Trans., 1902, 81, 590).

Maclurin, $C_{13}H_{10}O_6$.—When morin is precipitated from a hot aqueous extract of old fustic by means of lead acetate the solution contains maclurin. After removal of lead in the usual manner, the liquid is partially evaporated and extracted with ethyl acetate, which dissolves the colouring matter. The crude product is crystallised from dilute acetic acid (Perkin and Cope).

A description of maclurin and its derivatives will be found in the chapter devoted to benzophenone compounds.

Dyeing Properties of Old Fustic.—In silk and cotton dyeing fustic is employed to a comparatively limited extent, but in wool dyeing it is the most important natural yellow dyestuff. The olive-yellow or old-gold colours which fustic yields when used with chromium mordant and the greenish-olives obtained with the use of copper and iron mordants are all fast to light and milling, but the yellow colours yielded in conjunction with aluminium and tin possess only a moderate degree of fastness with respect to light. Fustic is chiefly employed in wool dyeing with potassium dichromate as the mordant, and it is for the most part used along with other dyestuffs, e.g. logwood, alizarin, etc., for the production of various compound colours, olive, brown, drab, etc.

Osage Orange Tree.

Though the wood of this tree has been used for many years in a desultory manner for dyeing by the Indians in the Red Valley region of Texas, America, its employment as a dyestuff has only recently engaged the attention of the United States Forest Service. As the result of its examination by Kressmann (Journ. Amer. Leather Chemists Association, 1915, 347), it has been found that its dyeing properties are very similar to those given by old fustic, the shades which it produces being, however, slightly purer and somewhat less red in tint. A qualitative study of the aqueous extract showed that the dyeing principles present consisted as in old fustic of *morin* and *maclurin*, but that the unknown red constituent present in this latter was practically absent. Though apparently the tinctorial strength of distinct samples of the osage orange wood is somewhat variable, this is probably on the average quite equal to that of old fustic, and this wood can be satisfactorily employed not only for textile but also for leather dyeing.

Jak-wood.

Jak-wood, or Jack-wood, is derived from the *Artocarpus integrifolia* (Linn.) which belongs to the *Urticaceæ*, and is cultivated

throughout India, Burmah, and Ceylon, except in the north. It is largely used for carpentry, furniture, etc., and is stated to be imported to Europe for this purpose. The rasped wood is used by the natives of India and Java as a yellow dye in conjunction with alum, for the robes of the Burmese priests, also for dyeing silk and for general purposes.

An aqueous solution of the wood possesses the characteristic property that when it is treated with alkali and gently warmed, the yellow solution at first obtained assumes a beautiful blue tint.

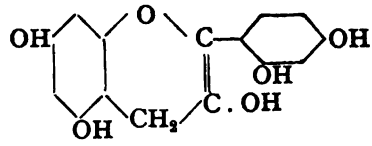
Jack-wood (Perkin and Cope, Chem. Soc. Trans., 1895, 67, 937) is very similar to old fustic, and its dyeing properties are due to *morin* (see Old Fustic). Unlike old fustic, however, it contains no maclurin, but there is present a second substance, *cyanomaclurin*, which is devoid of tinctorial property. These compounds can be isolated from jack-wood by methods which are almost identical with those which have been applied to fustic itself, and their separation may be effected by means of lead acetate as this precipitates only the morin.

Cyanomaclurin, $C_{15}H_{12}O_6$, crystallises in colourless prisms, somewhat readily soluble in water, and gives with basic lead acetate a colourless precipitate, and with ferric chloride a violet coloured liquid. Its solution in dilute alkalis is colourless, but if this be gently warmed a beautiful deep indigo coloration is produced, which on longer digestion passes into green and finally becomes brown-yellow. When fused with alkali, it gives *β-resorcylic acid* and *phloroglucinol*.

Acetylcyanomaclurin, $C_{15}H_7O_6(C_2H_3O)_5$, colourless needles, melts at 136—138°, and *benzoylcyanomaclurin*, $C_{15}H_7O_6(C_7H_5O)_5$, colourless prisms, melts at 171—172°. *Disazobenzenecyanomaclurin*, $C_{15}H_{10}O_6(C_6H_5N_2)_2$, scarlet needles, melting-point 245—247° (decomp.), gives an *acetyl* derivative probably

$$C_{15}H_7O_6(C_6H_5N_2)_2(C_2H_3O)_3,$$

orange-red needles, melting-point 209—210° (decomp.) (Perkin, Chem. Soc. Trans., 1905, 87, 715). In certain respects, cyanomaclurin resembles the catechins of gambier and acacia catechus, and more especially so in that by boiling with dilute acids it gives reddish-brown amorphous substances, which are very similar to the so-called catechin anhydrides. The product obtained by the action of hydrochloric acid on a boiling acetic acid solution of cyanomaclurin is insoluble in alkalis and all solvents, and has a percentage composition almost identical with the catechin anhydride similarly produced. According to Perkin, cyanomaclurin is possibly a reduction product of morin, thus :—



Jack-wood dyes shades very similar to those given by old fustic; that is, olive-yellow with chromium, dull yellow with aluminium, and a brighter yellow with tin mordant. On the other hand, the sample examined by Perkin and Cope possessed only about one-third of the dyeing power of old fustic.

MYRICA NAGI.

Myrica nagi (Thunb.).—This is an evergreen tree belonging to the *Myricaceæ* met with in the sub-tropical Himalaya from the Ravi eastwards, also in the Khasia mountains, the Malay Islands, China, and Japan. It is the box-myrtle or *yangmæ* of China, and is synonymous with *M. sapida* (Wall.), *M. rubra* (Sieb. and Zucc.) and *M. integrifolia* (Roxb.). The bark is occasionally used as a tanning agent, and is said to have been exported from the North-West Provinces to other parts of India to the extent of about 50 tons per annum. In Bombay it is met with under the name of *kaiphal*, and in Japan as *shibuki*.

Myricetin, $C_{15}H_{10}O_8$, H_2O, the colouring matter, can be isolated from an aqueous extract of the plant by a similar method to that which is serviceable for the preparation of fisetin (see Young Fustic), but is more readily obtained in quantity from the Japanese commercial "shibuki" extract (Perkin and Hummel, Chem. Soc. Trans., 1896, 69, 1287; and Perkin, *ibid.*, 1902, 81, 204).

The extract is treated with ten times its weight of hot water to remove tannin, and when cold the clear liquid is decanted off, the residue washed twice in a similar manner, and well drained. The product is extracted with boiling alcohol, and the solution evaporated until crystals commence to separate. On cooling these are collected (the filtrate A being reserved) and washed first with strong and then with dilute alcohol. A complete purification is best effected by converting the colouring matter into its acetyl derivative, and when pure hydrolysing this in the usual manner. Myricetin crystallises in yellow needles, melting at about 357°, and closely resembles quercetin in appearance. Dilute potassium hydroxide solution dissolves myricetin with a green coloration, which, on standing in air, becomes first blue, then violet, and eventually brown coloured. Alcoholic lead acetate

gives an orange-red precipitate, and ferric chloride a brown-black coloration.

With mineral acids in the presence of acetic acid the following compounds which crystallise in orange-red needles have been prepared :—

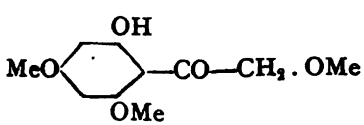
Myricetin sulphate, $C_{15}H_{10}O_8 . H_2SO_4$, *myricetin hydrochloride*, $C_{15}H_{10}O_8 . HCl$, *myricetin hydrobromide*, $C_{15}H_{10}O_8 . HBr$, and *myricetin hydriodide*, $C_{15}H_{10}O_8 . HI$. Alcoholic potassium acetate yields *monopotassium myricetin*, $C_{15}H_9O_8K$. Bromination in the presence of alcohol gives *tetrabrom-myricetin ethyl ether*, $C_{15}H_5O_8Br_4Et$, colourless needles, melting-point about 146° (Perkin and Phipps, *ibid.*, 1904, 85, 62), and this is analogous to the behaviour of morin under similar circumstances. By the action of bromine in acetic acid *tetrabrom-myricetin*, $C_{15}H_6O_8Br_4$, brown-red needles, melting-point 235—240°, is produced.

When fused with alkali myricetin gives *phloroglucinol* and *gallic acid*. *Hexa-acetylmyricetin*, $C_{15}H_4O_8(C_2H_3O)_6$, colourless needles, melting-point 211—212°; *hexabenzoylmyricetin*, $C_{15}H_4O_8(C_7H_5O)_6$, colourless needles; *myricetin pentamethyl ether*, $C_{15}H_5O_3(OCH_3)_5$, pale yellow needles, melting-point 138—139°; *acetylmyricetin pentamethyl ether*, $C_{15}H_4O_3(OCH_3)_5C_2H_3O$, colourless needles, melting-point 167—170°, have been prepared. *Myricetin hexamethyl ether*, $C_{15}H_4O_2(OCH_3)_6$, colourless needles, melting-point 154—156°; and *myricetin hexaethyl ether*, $C_{15}H_4O_2(OC_2H_5)_6$, almost colourless needles, melting-point 149—151°, may be obtained by means of methyl and ethyl iodides respectively.

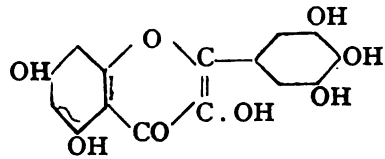
Myricetin dyes mordanted woollen cloth the following shades, which are practically identical with those given by quercetin :—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Red-brown.	Brown-orange.	Bright red-orange.	Olive-black.

On digestion with alcoholic potash at 170° myricetin pentamethyl ether gives *gallic acid trimethyl ether* and *phloroglucinol monomethyl ether*, whereas myricetin hexaethyl ether gives *gallic acid triethyl ether* and *phloroglucinol diethyl ether*. With boiling alcoholic potash myricetin hexamethyl ether gives gallic acid trimethyl ether and *methoxy fisetol dimethyl ether* (Perkin, Chem. Soc. Trans., 1911, 100, 1721)—



Myricetin hexaethyl ether behaves similarly with production of gallic acid triethyl ether and *ethoxy fisetol diethyl ether*, prismatic needles, melting-point 96—97°. Myricetin is therefore a *hydroxy quercetin*, and possesses the following constitution :—



Myricitrin, $C_{21}H_{22}O_{13}$, H_2O, or rather $C_{21}H_{20}O_{12}$, $2H_2O$, the glucoside, is present in the alcoholic filtrate A, from the crude myricetin, from which it separates on standing. The crystals are collected, washed first with alcohol, then with dilute alcohol, crystallised from water, from alcohol, and finally from water. Myricitrin forms pale yellow, almost colourless leaflets, melting at 199—200°, and is soluble in alkalis with a pale yellow tint. Aqueous lead acetate gives an orange-yellow precipitate, and alcoholic ferric chloride a deep greenish-black coloration. In appearance it cannot be distinguished from quercitrin, and the shades given by the two substances on mordanted woollen cloth are practically identical.

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Full brown-yellow.	Full golden-yellow.	Lemon-yellow.	Brown-olive.

When hydrolysed with dilute sulphuric acid myricitrin yields rhamnose and myricetin, according to the equation—

$$C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_8 + C_6H_{12}O_5,$$

and is analogous to quercitrin which in a similar manner gives rhamnose and quercetin. In addition to myricetin the *M. nagi* contains a trace of a glucoside of second colouring matter, which is probably *quercetin*.

The *dyeing properties* of myrica bark are generally similar to those of other yellow mordant dyestuffs. On wool with chromium mordant it gives a deep olive-yellow, and with aluminium a dull yellow, similar to the colours obtained from quercitron bark, but much fuller; with tin mordant it gives a bright red-orange, redder in hue than that given by quercitron bark; with iron mordant it gives a dark greenish-olive like that obtained from quercitron bark, but again fuller.

On cotton with aluminium and iron mordants it dyes colours which are more similar to those obtained from old fustic than from quercitron bark. Some specimens of myrica bark are exceedingly rich in colouring matter, and a sample examined by Hummel and

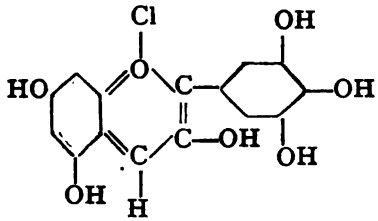
Perkin (J. Soc. Chem. Ind., 1895, 14, 458) possessed much stronger dyeing power than old fustic.

According to Satow (J. Ind. Eng. Chem., 1915, 7, 113) (Abst. Chem. Soc., 1911, 149), the colouring matter of the *M. rubra* has the formula $C_{15}H_{10}O_8$, and is identical in some of its properties with myricetin. By fusion with sodium polysulphide and sulphur a product is obtained which dyes cotton a deep sepia colour, though if copper sulphate, manganese sulphate, or ferrous sulphate is added to the fused mass, substances possessing a bluish or bluish-grey colour are produced. By fusing myricetin with sulphur alone a brown-yellow compound is obtained. A yellow dye may also be obtained by nitrating myricetin sulphonic acid.

Other Sources of Myricetin.

Sicilian sumach, the leaves of the *Rhus coriaria* (Linn.), contain myricetin, probably as glucoside (Perkin and Allen, *ibid.*, 69, 1299). The colouring matter also exists in *Venetian sumach*, *R. cotinus*, and this is interesting, because the wood of this tree constitutes "young fustic" and contains fisetin. Among other plants myricetin has been isolated from the *Myrica gale* (Linn.), the leaves of *Pistacia lentiscus* (Linn.), the leaves of the logwood tree, *Hæmatoxylon campechianum* (Linn.), and it is found in conjunction with quercetin in the leaves of the *Coriaria myrtifolia* (Linn.) and the *R. metopium* (Linn.).

Everest (Royal Soc. Proc., 1918, B., 90, 251 (has shown that in all probability myricetin—as a glucoside—accompanies the anthocyanin pigment Violanin; a glucoside of



in the flowers of the purple-black viola (Sutton's "Black Knight"), an observation which is of considerable interest in connection with the relationship which exists between the flavonols and anthocyans.

Cotton Flowers.

Among the various portions of the cotton plant which have been industrially employed must be included the flowers which constitute one of the numerous Indian dyestuffs. According to Watt

("Dictionary of the Economic Products of India") they are thus used in the Manipur district. *Gossypetin* was first isolated in small quantity from the flowers of the ordinary Indian cotton plant, *G. herbaceum* (Perkin, Chem. Soc. Trans., 1899, 75, 826), and has been more completely studied at a later period (*ibid.*, 1913, 103, 650). For its preparation a concentrated alcoholic extract of the flowers is treated with hot water and the mixture digested when boiling with addition of hydrochloric acid for three hours. After removal of tar by filtration the hot liquid on cooling deposits a brownish-yellow powder, which contains a mixture of quercetin and gossypetin. These colouring matters are separated by a fractional crystallisation of their mixed acetyl derivatives from acetic anhydride, acetylgossypetin being in these circumstances the least soluble. The acetyl compound is finally hydrolysed by sulphuric acid in the presence of acetic acid in the ordinary manner.

Gossypetin, $C_{15}H_{10}O_8$, forms yellow needles, melting-point 311—313°, closely resembles quercetin in appearance, and is readily soluble in alcohol, but only very sparingly soluble in water. Concentrated alkaline solutions dissolve it forming orange-red liquids which on agitation and dilution with water, become green, then blue, and finally assume a dull brown tint. Alcoholic lead acetate gives a deep red precipitate in the cold passing into dull brown at the boiling-point, and with alcoholic ferric chloride a dull olive-green liquid is obtained.

Gossypetin like quercetin forms compounds with mineral acids which crystallise in orange-red needles, and with alcoholic potassium acetate the *monopotassium* derivative $C_{15}H_9O_8K$ is produced. The *hexa-acetyl* derivative $C_{15}H_4O_8(C_2H_3O)_6$ forms colourless needles, melting at 228—230°. By fusion with alkali or by dissolving the colouring matter in cold 50 per cent. aqueous potassium hydroxide and allowing the solution to remain exposed to air for twenty-four hours, with shaking, *protocatechuic acid* is obtained. A phenolic substance also produced by these methods of hydrolysis has not yet been identified.

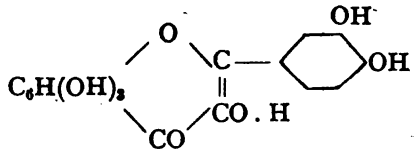
When methylated with excess of methylic iodide and methyl alcoholic potash *gossypetin hexamethyl ether*, $C_{15}H_4O_2(OMe)_6$, colourless needles, melting-point 170—172°, is produced, and this by hydrolysis with alcoholic potash gives *protocatechuic acid dimethyl ether* and *gossypitol tetramethyl ether*, $C_{12}H_{16}O_6$, needles, melting-point 115—116°. By ethylation in a similar manner, *gossypetin hexaethyl ether*, $C_{15}H_4O_2(OEt)_6$, melting-point 144—146°, can be prepared, and with alcoholic potash yields *diethylprotocatechuic acid* and *gossypitol tetra-*

ethyl ether, $C_{16}H_{24}O_6$, melting-point 110—111°. The latter forms an *oxime*, $C_{16}H_{25}O_6N$, melting-point 127—129°, and when oxidised with permanganate gives *gossypetonic acid*, yellow needles, melting-point 154—155°. The constitutions assigned both to this latter (1) and to gossypitol tetraethyl ether (2) are given below:—

(1) $HO.C_6H(OEt)_3CO.CO_2H$

(2) $HO.C_6H(OEt)_3CO.CH_2.OEt$

and from these that of gossypetin naturally follows:—



When an alkaline solution of gossypetin is exposed to air the blue liquid on acidification yields a reddish-brown precipitate which on gentle warming becomes crystalline. Again, if benzoquinone is added to a solution of gossypetin in cold absolute alcohol a similar reaction takes place. On keeping for a few minutes crystals commerce to separate and by then heating to 50° a semi-solid mass is obtained.

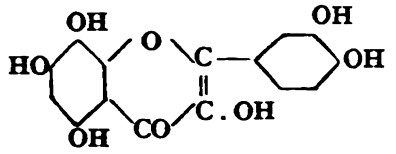
Gossypitone, $C_{15}H_8O_8$, the name assigned to this substance, consists of microscopic needles of a dull red colour, which are difficultly soluble in the usual solvents. It dissolves in dilute alkalis with a pure blue coloration and its solution in concentrated sulphuric acid is dull brown. Sodium hydrogen sulphite solution reconverts it into gossypetin. Gossypitone possesses strong dyeing properties, and gives the following shades on mordanted woollen cloth:—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Dull-brown.	Orange-brown.	Orange-red.	Deep olive.

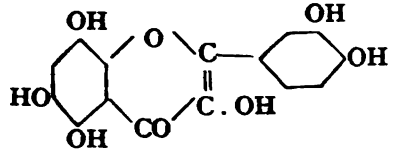
These, it is interesting to note, are identical with those given in these circumstances by gossypetin itself, and it is accordingly evident that during the dyeing operation oxidation of the latter to gossypitone takes place. Until a definite knowledge of the tetrahydroxybenzene nucleus in gossypetin has been obtained the position of the hydroxyl groups in this portion of the molecule can only be conjectured. Existing as it does side by side with quercetin it seems natural to consider that gossypetin is a hydroxyquercetin. Again, should gossypitone be a *p*-quinone, the constitution of gossypetin will be the same as that which Neirenstein and Wheldale have suggested (Ber., 1911, 48, 3487) for the flavonol described earlier (1) which they obtained from quercetone, but the descriptions of the two compounds are not

in agreement.* On the assumption of the necessity for a quinol nucleus in gossypetin a second constitution (2) is however possible :—

(1)

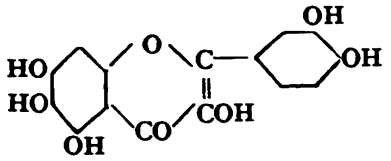


(2)



Again, a third expression (3), representing gossypetin as an hydroxyquercetin, is available, though in this case gossypitone must be regarded as an ortho- rather than a para-quinone :—

(3)



The glucosides present in cotton flowers have been examined by Perkin (Chem. Soc. Trans., 1909, 95, 2181), who in the first place employed the Egyptian variety. The Egyptian cottons appear according to the researches of Messrs. Fletcher and Balls to be derived from natural crosses of brown Peruvian cottons with the Sea Island variety.

A concentrated alcoholic extract of the flowers deposits on cooling a semi-crystalline powder, and this consists mainly of the potassium salts of two glucosides, quercimeritrin and gossypitrin, whereas a third glucoside iso-quercitrin is present in the filtrate. A rough separation of the latter from this mixture may also be effected by means of aqueous lead acetate, for in these circumstances the precipitation of isoquercetin does not occur, at least to any extent. The isolation of quercimeritrin and especially of gossypitrin in a pure condition from these flowers is however of too tedious a character to be described here, and for details of the processes involved the original paper must be consulted.

* This compound, more recently synthesised by Neirenstein (Chem. Soc. Trans., 1915, 107, 872), is described as melting at 354—355°, and its hexamethyl ether at 145—147°.

Quercimeritrin, $C_{21}H_{20}O_{12}$, $3H_2O$, melting-point 247—249°, consists of small, glistening, bright yellow plates, insoluble in cold and fairly readily soluble in boiling water. Its alkaline solutions possess a deep yellow tint; with aqueous lead acetate it gives a bright red precipitate, and with ferric chloride an olive-green coloration. *Octa-acetylquercimeritrin*, needles, $C_{21}H_{12}O_{10}(C_2H_3O)_8$, melting-point 214—216°, is sparingly soluble in alcohol, whereas *monopotassium quercimeritrin*, a yellow powder, can be obtained by means of alcoholic potassium acetate. By hydrolysis with dilute sulphuric acid quercimeritrin yields quercetin and glucose according to the following equation:—

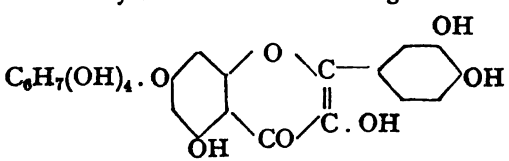
$$C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$$

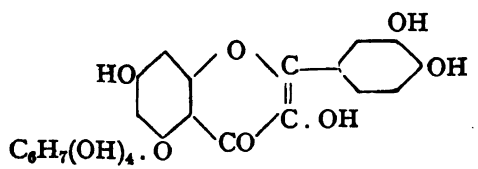
and is thus analogous to quercitrin which in this manner is converted into quercetin and rhamnose.

On wool mordanted with aluminium, tin, chromium, and iron, quercimeritrin gives the following shades:—

Aluminium.	*Tin.*	*Chromium.*	*Iron.*
Orange-yellow.	Bright orange.	Reddish-brown.	Olive-brown.

and these results are interesting, because with the exception of the iron mordanted pattern, which is of a rather browner character, the colours thus produced closely resemble those which are given by quercetin itself when dyed in a similar manner. They are widely different from those given by rutin and quercitrin, and mainly as a result of this property there can be little doubt that quercimeritrin is to be represented by one of the two following formulæ:—





Quercimeritrin is also present in the flowers of the *Prunus emarginata*? (Finnemore, Pharm. Jour., 1910, (iv.), 31, 604).

Gossypitrin, $C_{21}H_{20}O_{13}$, only isolated with considerable difficulty, is more readily prepared from the *G. neglectum* (see below). When crystallised from dilute acetic acid it contains $2H_2O$ of crystallisation,

and is readily dissolved by hot water, but on boiling this solution yellow needles of the anhydrous substance, melting-point 240—242°, separate. When anhydrous it does not absorb water of crystallisation from moist air, but on boiling with acetone the hair-like needles are broken up into much finer needles, which when dried at 100° possess 1 molecule of water of crystallisation. Such a preparation melts at 200—202°, and when dried at 160° on standing in air now absorbs water. Preparations possessing this lower melting-point can be obtained in other ways, and it is accordingly evident that gossypitrin exists in two interchangeable modifications.

Gossypitrin dissolves in alkalis with a pale yellow coloration, and gives with lead acetate a deep red precipitate. It is almost insoluble in boiling acetone, a property which readily distinguishes it from quercimeritrin, which is fairly soluble in the latter solvent.

Acetyl gossypitrin, $C_{21}H_{11}O_{13}(C_2H_3O)_9$, colourless needles, melting-point 226—228°, is almost insoluble in alcohol.

When hydrolysed with dilute sulphuric acid gossypitrin yields gossypetin and dextrose according to the equation—

$$C_{21}H_{20}O_{13} + H_2O = C_{15}H_{10}O_8 + C_6H_{12}O_6$$

The shades given by this glucoside on mordanted wool are as follows:—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Reddish-brown.	Dull yellow.	Bright orange.	Dark olive-brown.

Gossypitrin reacts, like gossypetin itself, with benzoquinone, and yields in this way a quinone to which the name *Gossypitrone*, $C_{21}H_{18}O_{13}$, has been assigned. This consists of maroon coloured needles, which possess no definite melting-point, although fusion of the product occurs about 255—259°. By the action of warm dilute sulphurous acid solution it is reconverted into gossypitrin, and the same change appears to occur in the dyeing process, for the shades produced are identical with those yielded by this latter glucoside. It is considered probable that the sugar group of gossypitrin is attached to its tetrahydroxybenzene nucleus, though until the exact nature of this has been decided, its position is necessarily uncertain.

Isoquercitrin, $C_{21}H_{20}O_{12}$, $2H_2O$, crystallises from dilute alcohol in pale yellow needles, melting at 217—219°. It is sparingly soluble in water, and dissolves in alkaline solutions with a deep yellow tint, but its most interesting property is the fact that with aqueous lead acetate solution it gives a bright yellow precipitate entirely distinct

from the deep red deposit which is produced in this manner from the isomeric quercimeritrin.

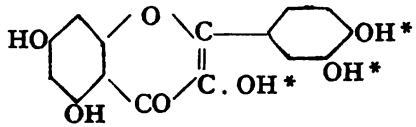
Again, though more readily susceptible to hydrolysis than the latter glucoside, it yields identical products:—

$$C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$$

Dyeing experiments with isoquercitrin give shades entirely distinct from those given by quercimeritrin, and these, although slightly paler, resemble those yielded by quercitrin.

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Brownish-yellow.	Golden-yellow.	Lemon-yellow.	Brownish-olive.

The properties of this substance indicate that its sugar group is not attached as in quercimeritrin to the phloroglucinol nucleus of quercetin. Indeed it is probably constituted similarly to quercitrin (*loc. cit.*), which, however, contains a rhamnose in the place of the glucose residue. Three formulæ are possible for isoquercitrin, which may be briefly expressed by the statement that the position of the sugar residue in respect to the quercetin group is at one or other of the points in the following which are marked with an asterisk:—



The aqueous extract of the Egyptian cotton flowers employed in this investigation gave by hydrolysis with acid 1·86 per cent. of crude colouring matter, and in this approximately 10 per cent. of gossypetin was present. Dyeing experiments with the flowers in the usual way gave the following shades:—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Reddish-brown.	Green-yellow.	Orange-brown.	Olive-brown.

and these though duller were somewhat similar in character to those given by quercimeritrin. In comparison with the shades similarly produced from other natural dyes, they most nearly resemble those of the so-called "Patent Bark," a preparation of quercitron bark in which quercetin and no quercitrin is present.

Among the types of cotton flowers there are (*a*) red, (*b*) pink, (*c*) yellow, and (*d*) white flowered plants. In the offspring of a cross between (*a*) and (*c*) there occurs in the second and subsequent generations red and yellow plants which breed pure, whereas in the off-

spring of a cross between (*a*) and (*d*) all four forms occur which breed pure. As a supplementary investigation to that of the Egyptian flowers the petals derived from such pure plants occurring among the offspring of one or other of these crosses have been examined (Perkin, Chem. Soc. Trans., 1916, 109, 145), (cp. Leake, Proc. Roy. Soc., 1911, (B), 83, 147).

The types were as follows: red flowered, *G. arboreum* (Linn.); pink, *G. sanguineum* (Harsk); yellow and white, two varieties of *G. neglectum* (Tod), usually now treated as one species but originally described as *G. neglectum* and *G. rossrum*. As a result it has been found that the red flowers of *G. arboreum* contain *isoquercitrin*, quercimeritrin and gossypitrin in this case being absent, whereas in the yellow flowers of *G. neglectum*, *gossypitrin* and *isoquercitrin* were present, and quercimeritrin appeared to be absent. On the other hand, the white flowers of *G. neglectum* and the pink flowers of *G. sanguineum* gave but traces of colouring matter too small for complete identification, though the respective products obtained resembled in their properties apigenin and quercetin. An examination of the ordinary Indian cotton flower, *G. herbaceum*, available only in small amount, gave the same results as the *G. neglectum*.

Gossypetin is also present in the flowers of the *Hibiscus sabdariffa* or "red sorrel" of the West Indies, a small shrub which is widely cultivated throughout the hotter parts of India and Ceylon (Perkin, Chem. Soc. Trans., 1909, 95, 1855). The stems yield the "Rozelle hemp" of commerce, and this is obtained by retting the twigs as soon as the plant is in flower. The yellow flowers are just capable of dyeing yellow but are not used at all in India for this purpose; on the other hand, the red calyces are employed for dyeing in an obscure degree in two remote parts of the country (Burkill, Agricultural Ledger, Calcutta, 1908, No. 2, 13).

African Marigold. Tagetes patula.

Quercetagetin was isolated from the flowers of the African marigold, *Tagetes patula*, by Latour and Magnier de la Source (Bull. Soc. Chim., 1877, (ii.), 28, 337), who state that it also occurs in other varieties of the same plant. In appearance and general properties it is described as resembling quercetin, the colouring matter of quercitron bark, and from this fact, together with its origin, the name *quercetagetin* is evidently derived. On the other hand, according to these authors, its crystalline form, solubility in 60 per cent. alcohol, and the numbers obtained on analysis indicated that it was distinct from quercetin $C_{27}H_{20}O_{12}$, and it was considered to possess

the formula $C_{27}H_{22}O_{13}$ (anhydrous) or $C_{27}H_{22}O_{13}$, $4H_2O$ (air-dried). A preliminary re-examination of this colouring matter was made by Perkin in 1902 (Chem. Soc. Proc., 18, 75), and it has more recently been studied in greater detail by the same author (Chem. Soc. Trans., 1913, 103, 209). To isolate the colouring matter, which is largely present in the flowers as glucoside, a concentrated alcoholic extract is diluted with water which precipitates a viscous impurity, and this is removed by means of ether. The clear liquid treated when boiling with addition of a little hydrochloric acid deposits after cooling but a small bulk of the colouring matter, and repeated extraction of the solution with ether is necessary for its economical isolation. The crude product thus obtained can be crystallised from dilute alcohol, but for complete purification it is necessary to prepare the acetyl derivative, and after re-crystallisation to hydrolyse this in the usual manner.

Quercetagetin, $C_{15}H_{10}O_8$, or as crystallised from dilute alcohol $C_{15}H_{10}O_8$, $2H_2O$, forms pale yellow glistening needles or leaflets resembling quercetin in appearance and melts at about 318°. Very dilute alkali dissolves it with a pure yellow colour, which by air oxidation becomes olive, and finally deep brown, but these changes are not so marked when a stronger alkali (10 per cent.) is employed. Alcoholic ferric chloride produces an olive-green coloration, whereas cold alcoholic lead acetate forms an orange-red precipitate which on keeping becomes yellower and finally develops a green tint. On fusion with alkali *protocatechuic acid* is obtained, together with a phenolic product which, however, quickly oxidises, and has not yet been identified.

Quercetagetin readily yields oxonium salts with mineral acids, and of these the *sulphate* $C_{15}H_{10}O_8$, H_2SO_4, fine orange coloured needles, has been described.

Monopotassium quercetagetin, $C_{15}H_9O_8K$, separates as an orange-yellow semi-crystalline precipitate when potassium acetate is added to a solution of quercetagetin in absolute alcohol.

By acetylation *acetylquercetagetin*, $C_{15}H_4O_8(C_2H_3O)_6$, colourless needles, melting at 209—211°, is produced, and on alkylation employing alkyl iodide *quercetagetin pentamethyl ether*,

$$C_{15}H_5O_3(OCH_3)_5,$$

pale yellow needles, melting-point 161—162°, and *quercetagetin hexamethyl ether*, $C_{15}H_4O_2(OCH_3)_6$, colourless needles, melting-point 157—158°, can be prepared. *Acetylquercetagetin pentamethyl ether*,

$$C_{15}H_4O_3(OCH_3)_5C_2H_3O,$$

melts at 161—163°.

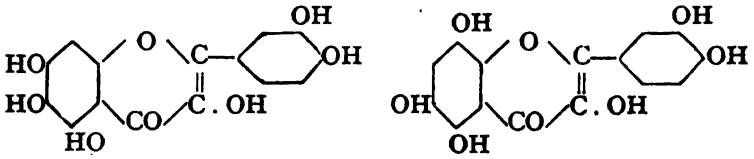
Quercetagetin hexaethyl ether, $C_{15}H_4O_2(OEt)_6$, melting-point 139—141°, yields oxonium salts with mineral acids in the presence of acetic acid, the sulphate separating in orange needles, whereas the crystals of the hydrochloride possesses a somewhat more yellow colour. This behaviour is analogous to that of quercetin pentamethyl ether (Watson, Chem. Soc. Proc., 1911, 27, 163).

When hydrolysed with alcoholic potassium hydroxide quercetagetin hexaethyl ether gives *protocatechuic acid diethyl ether* and *quercetagetol tetraethyl ether*, $C_{16}H_{24}O_6$, which crystallises in prismatic needles, melting-point 46—48°. The latter yields the oxime $C_{16}H_{25}O_6N$, melting-point 93—95°, and when oxidised with alkaline permanganate *quercetagetinic acid*, melting-point 100—102°, is produced.

The production of quercetagetol diethyl ether to which the constitution (1) is assigned, and protocatechuic acid diethyl ether (2)

(1) $C_6H(OEt)_3\begin{cases}OH\\ CO—CH_2\,.\,OEt\end{cases}$ (2) $CO_2H\,.\,C_6H_3(OEt)_2$

from quercetagetin hexaethyl ether, indicate that quercetagetin is a pentahydroxyflavonol isomeric with myricetin and gossypetin. Similarly to this latter colouring matter it appears to contain a tetrahydroxybenzene nucleus, and it is suggested that its constitution may be represented by one of the two following formulæ :—



Quercetagetin readily dyes mordanted fabrics shades of a generally similar character to those given by other well-known flavonol colouring matters.

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Dull olive-yellow.	Yellow-orange.	Brown.	Brownish-black.

A trace of a more sparingly soluble colouring matter is present in the flowers and represents about 1 per cent. of the crude quercetagetin referred to above. It crystallises from alcohol in somewhat indefinite groups of minute needles and dissolves in alkaline solutions with an orange colour passing to green on dilution with water. Though similar in appearance to rhamnetin (quercetin monomethyl ether) it does not contain a methoxy group.

Dyeing Properties of the Flowers.—Employing mordanted woollen cloth, the following shades are produced :—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Yellowish-brown.	Pale dull yellow.	Deep yellow-orange.	Brownish-black.

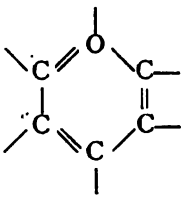
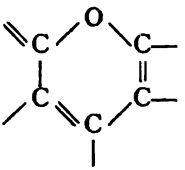
These possess a somewhat redder character than those given by quercitron bark, and are similar to, though not so red as those from patent bark. As quercetagetin mainly occurs in the flowers as glucoside, their tinctorial effect is evidently due to this latter.

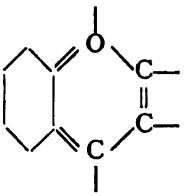
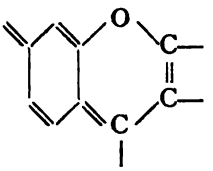
CHAPTER VIII.

γ-PYRAN GROUP.

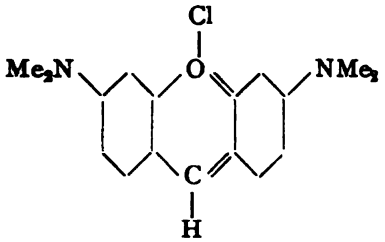
Anthocyanins and Anthocyanidins. *The Anthocyan Pigments: Introduction*—Historical — Structure and Relationship to Flavonols — Tinctorial Properties. *Pelargonidin:* Callistephin — Pelargenin — Pelargonin — Salvianin—Salvin—Salvinin. *Cyanidin:* Asterin — Chrysanthemin — Idaein — Cyanin — Mekocyanin — Keracyanin — Prunicyanin — Peonidin — Peonin. *Delphinidin:* Violanin — Delphinin — Ampelopsidin — Ampelopsin — Myrtillidin—Myrtillin—Althaein—Petunidin—Petunin—*Vitis riparia* Pigments —Malvidin—Malvin—Oenidin—Oenin. *Synthetic Products of the Anthocyan Series.* Other members of the group: Carajura—*Bignonia tecoma.*

THE γ-PYRAN, OR BENZOPYRANOL GROUP—INTRODUCTION.

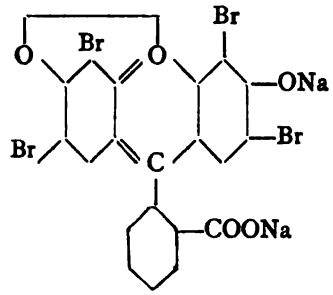
The groups,  or 

and  or 

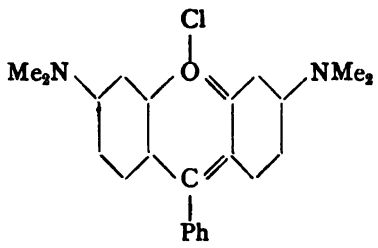
are of considerable interest in connection with both the artificial and naturally occurring colouring matters. They form the basis of a number of synthetic colours that have been in commercial use for many years, of which the following may be cited as typical instances:—



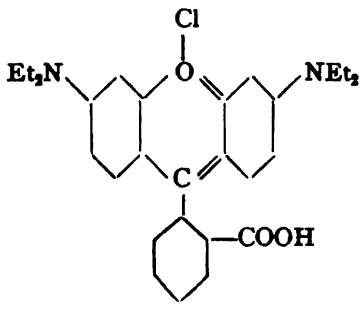
Pyronin G.



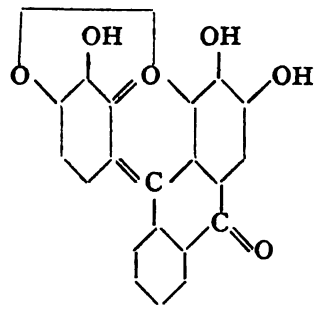
Eosin A.



Tetramethylrosamine.



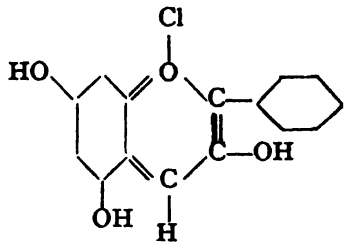
Rhodamine B.



Coerulein.

whilst related to these, but of less value, are such products as the succineins and sacchareins.

The result of recent researches upon naturally occurring colouring matters has been that a large number of substances, the anthocyans, colours of great beauty and widely distributed in nature, are now known to be derivatives of the benzopyranol complex; indeed all the products of this group as yet investigated are derived from the following nucleus—



by the introduction of further hydroxyl groups.

Interest in this type of compound is increased by the fact that compounds related to the anthocyans have been synthetically prepared which have rather more useful tinctorial properties than those possessed by the natural colours, and it is not impossible that the number of commercially useful derivatives in which the γ-pyran nucleus is present may be further increased by work that may follow upon the recent researches in this field.

The Anthocyan Pigments—Introduction.

The red, blue, and purple pigments of this group being the cause of some of nature's most beautiful and vivid colour effects, it is not at all surprising that at quite an early date chemists began to attempt the investigation of these pigments. Despite this, it is only within the last few years that anything definite concerning the chemistry of this group has become known.

The term *Anthocyan* appears to have been introduced by Marquart (Die Farben der Blüten, Bonn, 1835) to designate the blue pigments present in flowers. Later there arose the belief that the red and purple flower pigments were all merely different forms of the same blue anthocyan—or, as Fremy and Cloëz styled it, *cyanin*—and that the variation of colour was merely due to the nature of the cell sap; this resulted in the name anthocyan being indiscriminately applied to all of them. The present use of the term anthocyan to designate a large class of naturally occurring plant pigments gradually became general as from time to time evidence accumulated to show that the red, purple, and blue pigments differed considerably among themselves.

As early as 1836, Hope, in a paper read before the Royal Society of Edinburgh (March 21; cf. J. f. prakt. Chem., (10), 269 (1837)), concluded, as the result of experiments on a large number of different kinds of flowers, that the pigments, or chromules, present were formed from faintly coloured chromogens, by a variety of changes.

Of these chromogens, according to Hope, there were two types, one called by him *Erythrogen*, which by the action of acids yielded red pigments, and a second, named by him *Xanthogen*, which with alkalis gave rise to yellow pigments. He concluded that, in orange, red, purple, and blue flowers both were present, whereas in yellow and white flowers only xanthogen was found. From his examination of leaves, he concluded that chlorophyll was accompanied by xanthogen, but that, excepting in cases where reddening was obvious—e.g. autumn leaves—no erythrogen was present.

In the following year, Berzelius (Annalen, 1837, 21, 262) published the results of experiments on the pigments present in some berries, as cherry, black-currant, and in autumn leaves, e.g. red-currant, and of his attempts to purify and isolate them. For the red-leaf pigments he suggested the name *Erythrophyll* (leaf red), but pointed out that there might be objections to this term, as the pigments of flowers and berries appeared to belong to the same class, —an indication of the expansion of the term anthocyan to cover other than flower pigments.

In his attempts to prepare the pure pigments, Berzelius made use of the precipitation, by means of lead acetate, of the insoluble lead salts of these pigments, and of their regeneration by means of sulphuretted hydrogen. Berzelius did not obtain any pure pigments, but the above-mentioned method, either as used by him, or with such small modifications as the decomposition of the lead salt by means of hydrochloric acid instead of with sulphuretted hydrogen, has been employed by a large number of later workers, though by this means only Grafe (1906) and Willstätter (1916) have succeeded in obtaining crystalline products. Berzelius was not of the opinion that all these pigments could be considered as the same blue substance changed by variation in the cell sap.

The next work of interest was that of Morot (Annales des Sc. nat., (3), 13, 160 (1849-1850)) who attempted to prepare the blue pigment of the cornflower by repeated precipitation of its aqueous solutions by means of alcohol. He did not thus obtain a pure product, but the method is of interest in that, improved by the use of modern apparatus, it constitutes the first step of the process whereby Willstätter and Everest isolated the pure corn-flower pigment. Impurities containing nitrogen were present in Morot's products, and in the presence of nitrogen he saw a possible connection between this pigment and chlorophyll, but it should be noted that he was doubtful whether this nitrogen was really a

constituent of the pigment. He described the decolorisation on standing in solution which is characteristic not only of this, but also of nearly all anthocyans. That this decolorisation observed by Morot occurred in other cases was proved by the work of Fremy and Cloëz (Journ. de Ph. et de Chim., (3), 25, 249), who, moreover, by allowing such a decolorised solution to evaporate in the air, whereby the colour returned as the solution became concentrated, showed that the pigment was not destroyed by this change. They, however, looked upon the decolorisation as the result of a reduction of the pigment. These workers used the cornflower, violet, and iris for their experiments on blue pigments, and for those on red ones, the dahlia, rose, and peony. In each instance they attempted to purify the pigment by use of the lead salt, as described by Berzelius, but in no case, however, did they obtain a pure product.

Fremy and Cloëz discussed the general ideas then current regarding the plant pigments, and pointed out the uselessness of assuming, as so many workers about that time did, that a relationship existed between chlorophyll and the blue and yellow pigments, for, as pure chlorophyll had not then been obtained, and the flower pigments were almost uninvestigated, no reliable conclusions could be drawn. They suggested that all anthocyans were one and the same substance —which they called cyanin—and that the colour variations were due to the properties of the particular plant sap. They distinguished three flower pigments: (1) *Cyanin* (red or blue); (2) *Xanthins* (yellow, insoluble in water); (3) *Xantheïns* (yellow, soluble in water). Here a clear distinction is made between the carotin derivatives, corresponding to (2), and the flavone and flavonol derivatives, to (3), both of which occur as yellow flower pigments. These authors considered that (1) and (3) were in no way related to each other, for although they almost invariably found (3) occurring in flowers containing (1), they never observed a blue flower turn yellow, nor a yellow flower turn blue.

Filhol (Comptes rend., 39, 194; J. pr. Chem., 1854, 63, 78) investigated qualitatively a large number of flowers and confirmed previous workers' observations that yellow pigments—for which he retained the name Xanthogen—were present, not only in yellow and white, but also in red, purple, and blue flowers. He concluded that, with some few exceptions, all the red, purple, and blue pigments were derived from the same anthocyan. He examined the decolorisation of anthocyans in solution, and finding that the addition of acid caused the reappearance of colour, concluded that the decolorisation could not be the result of a reduction, as sug-

gested by Fremy and Cloëz. In his opinion this was due to the mixing of the pigments with other contents of plant cells, from which they were kept apart in the living plant.

Martens in 1855 (cf. Jahres., 1855, 657) attacked the problem from another point of view, attempting to elucidate the mode of formation of the anthocyans in plants. He further confirmed the presence of the yellow pigments, for which he used the name Xantheïn of Fremy and Cloëz in flowers containing anthocyan, and as the result of his work was led to put forward the hypothesis that both yellow and red pigments have their origin in a faintly yellow substance produced in the sap of all plants, which by oxidation, particularly under the influence of alkalis and light, produces the different yellow pigments, from which by further action of light and oxygen, the red pigments are formed. It is interesting to note that the relationship thus suggested by Martens as existing between the yellow pigments and the anthocyans is that which has been revived in more recent years by Wheldale; Keeble, Armstrong and Jones, and others (see below).

In 1859 Morren put forward the suggestion that the blue flower pigments (anthocyans) were the alkali salts of acids which in the free state are red, and for which he used the name *Erythrophyll* (cf. Berzelius). His conception of the blue pigments has been confirmed by recent work, but not so that regarding the red colouring matters.

A number of workers have, at different times, attempted to prepare pure anthocyan pigments by making use of their lead salts (cf. Berzelius); thus Glénard (Comptes rend., 47, 268; Jahres., 1858, 476), working with red wine, and using ethereal hydrochloric acid for the decomposition of his lead salt, obtained a pigment which he called Oenolin, and for which he put forward the nitrogen-free formula $C_{20}H_{16}O_{10}$. His preparation was, however, by no means pure. Senier (cf. Jahres., 1878, 970), using *Rosa gallica*, and decomposing the lead compound, suspended in alcohol, either by sulphuric acid or sulphuretted hydrogen, prepared a pigment, for the lead salt of which he gave the formula $C_{21}H_{29}O_{20}Pb_2$. Heise (cf. Chem. Zentr., 1889, 2, 953) by similar means prepared two pigments (A and B) from red wine, using sulphuretted hydrogen for decomposing the lead salts, and suggested that Glénard's compound was a mixture of these. His examination, however, was not complete. Glan (Dissertation, Erlangen, 1892), examining the pigment of the deep-red hollyhock, also obtained two products, and in 1894, Heise (cf. Chem. Zentr., 1894, 2, 846) further prepared two pigments (A and B) from the bilberry (in this case using ethereal hydrochloric acid to

decompose the lead salt), and obtaining them in a fairly pure, but amorphous condition, showed that the one (B) was a glucoside of the other (A). He gave analyses and formulæ, but these have proved to be incorrect, though the relative amount of glucose which he found to be present in his glucoside (B) has proved to be approximately accurate.

The result of this work of Heise and Glan was to produce a general tendency to consider that the anthocyan pigments were present in plants both as glucosides and non-glucosides, the former predominating somewhat. Molisch, in 1905, decided in favour of their being glucosides, but Grafe, who carried out a continuation of Molisch's work on a preparative scale, reverted to the earlier ideas. The results of recent work have definitely proved that in all investigated cases these pigments occur as glucosides possibly accompanied in a few instances (cf. Annalen, 1916, 412, 195) by a small percentage of sugar-free pigment, the non-glucosides isolated by the above workers being almost entirely the result of hydrolysis during their preparation.

In 1895 Weigert published (Jahrber. der k. k. önol. and pomol., Lehranstalt in Klosterneuburg, 1894-1895) a classification of the anthocyan pigments, thereby completely dispelling the one pigment idea that had so often been brought forward. As already stated, the views of earlier workers upon this point differed considerably; thus Berzelius was of the opinion that more than one anthocyan pigment existed, whereas Fremy and Cloëz considered that all red, violet, and blue flowers contained the same blue pigment (cyanin), its colour having been changed by the conditions prevailing in the various cell saps. Filhol, as also Wigand (Bot. Ztg., 1862, 123), likewise asserted that all red and blue flower colours were produced by different forms of one and the same anthocyan, and Hausen (Die Farbstoffe der Blüten und Früchten, Würzburg, 1884, p. 8) went still further, being of the opinion that not only all red colours in flowers, but also those in fruits, were due to one and the same pigment. Wiesner (Bot. Ztg., 1862, 392), however, cast considerable doubt upon the identity of all these compounds.

Weigert, as a result of the comparison of the behaviour of the anthocyan pigments with various reagents, in particular with regard to the colour of their lead salts, and the colour changes that took place on addition of acid or alkali, distinguished two classes of these compounds, the first—Wine-red group—such as gave blue or blue-green lead salts, and whose acidified solution, on addition of alkali became blue or blue-green; and a second—the Beetroot-red group—which gave red lead salts, and whose acid solution showed no change

of colour, or slight change to violet-red, on being made alkaline. The crude anthocyan pigments are, however, so varied in their reactions, that this simple classification of Weigert by no means covers all cases, for even by comparison only of the colour changes on acidification or on being made alkaline, and by formation of the lead compounds, quite a number of sub-groups can be observed.

Overton (Pring. Jahrber. f. wiss. Bot., 1899, 33, 222) also came to the conclusion that a considerable number of different anthocyan pigments existed.

In all the above-mentioned work, either qualitative results only were aimed at, or the preparations were amorphous and lacked the essential characteristics of chemically pure products. From these observations, however, it had become clear that in the anthocyans a large class of new pigments were awaiting chemical investigation, and moreover, in the light of the work of Heise and Glan, it was evident that at least certain of these must be looked upon as belonging to a class of nitrogen-free glucosides. This view was expressed by Molisch in 1905.

In 1903 two papers were published by Griffiths (Ber., 36, 3959; and Chem. News, 88, 249) which, had they been followed up, might have had considerably greater influence on this field of work than has been the case. He describes the preparation for the first time of an anthocyan in a crystalline condition. His work was carried out with geranium and verbena flowers, but the pigment obtained from the latter contained nitrogen and sulphur and was doubtless impure; that from the geranium contained neither of these elements, and was the only one analysed. His method of preparation consisted in extracting the petals with 90 per cent. alcohol, and after filtration evaporating *in vacuo*. The residue thus obtained was extracted with absolute alcohol, filtered, and the filtrate again evaporated *in vacuo*, when the pigment separated in crystalline form. He did not attempt to decide whether the pigment was a glucoside or not. The description of his experiments is very superficial and imperfect; thus, for example, the fact that a fresh 90 per cent. alcoholic extract of geranium petals has a fine scarlet colour, but passes in a few minutes to a practically colourless solution, which, however, regains its original colour as evaporation takes place, is not even mentioned.

Very different in character from these papers of Griffiths is the beautifully clear and descriptive publication of the botanist Molisch (Bot. Ztg., 1905, 145), and a greater incentive to research upon these pigments than lies in this paper one cannot easily imagine.

Molisch, after giving a summary of the literature dealing with the then very doubtful appearance of solid anthocyan pigments in plants, described how, on examination of a number of anthocyan-containing flowers and leaves, he found that these pigments existed not only in solution in the cell sap, but were, in many cases, present also in the solid state, sometimes as small spheres, sometimes as definitely crystalline formations. Of some of the more well-defined cases he gave illustrations. Having described the appearance of anthocyan crystals in the living plant, he followed up these observations with a description of his attempts to obtain crystals of these pigments outside the plant. In this in several cases (pelargonium, rose, *Anemone fulgens*) he was successful, and gave illustrations of the resultant microscopic crystals. Having thus established the fact that some of these pigments readily crystallise, he pointed out that it should not be difficult to prepare them in sufficiently large quantities for chemical examination. In a very slightly modified form, the method whereby Molisch obtained his crystals is so simple and certain, that it is worth describing. One or two petals of the flower are laid upon a piece of glass, slightly larger than a microscope slide and upon which are one or two drops of 75 per cent. acetic acid, the cell structure is then broken down by rolling a glass rod over them, leaving the petals flattened on the glass with the cell sap beside or upon them. Two or three more drops of 75 per cent. acetic acid are then placed on the petals, and a microscope slide pressed down upon them. The whole is then placed under a clock-glass (to ensure slow evaporation), and after some twelve to twenty-four hours crystals begin to appear, either round the edge of the slide, or round or on the petals. Scarlet pelargonium gives the best results and very rarely fails; in some cases, using these flowers, clusters of crystals may be obtained so large that they are readily discernible by means of the naked eye.

As mentioned above, Grafe was moved by the work of Molisch to attempt the chemical investigation of some of these pigments. He published three papers (Sitzber. k. Akad. d. Wiss., Vienna, 1906, 975; 1909, 1033; and 1911, 765); in the first he described experiments with red cabbage leaves and rose petals, from neither of which could he obtain any crystalline pigment; from the blue-black berries of *Ligustrum vulgare* he obtained a crystalline product, but was unable to obtain any agreement in his analyses of it, and finally, with the flowers of the hollyhock (*Althaea rosea*), he obtained two pigments, one crystalline, the other amorphous, of which he gave analyses. In each case he used the lead compound for the prepara-

tion of his pigment, and decomposed this by means of sulphuretted hydrogen. After separation of the hollyhock pigment in this manner, he further purified it by means of alcohol and ether.

To the crystalline compound he gave the formula $C_{14}H_{16}O_6$, the amorphous product $C_{20}H_{30}O_{12}$; he considered the latter to be a glucoside, as from it he obtained glucose by hydrolysis, but apparently did not examine the non-glucoside pigment produced by this reaction. In his second paper he continued his investigation of the hollyhock pigment, and discussed the formation of anthocyans in the plant. The third paper of the series contains an account of his further attempts to prepare the pigment of the red cabbage in a crystalline form. Despite the fact that Molisch had failed to obtain crystals by his method, Grafe attempted to produce them by using the same process on a larger scale. Failing in his attempts, he tried dialysis—previously used in other cases by Portheim and Scholl (Ber. deut. Bot. Ges., 1908, *26a*, 480)—as a means of purification, but again failed to obtain any crystalline product. Grafe then turned his attention to the pigment of the scarlet pelargonium, which had so readily yielded crystals. He was successful in obtaining this pigment in a fine crystalline condition (microphotographs of the crystals were given) by carrying out Molisch's experiment on a large scale, employing the lead salt method, or dialysis. Besides the crystalline pigment, Grafe obtained, as with the hollyhock, an amorphous compound, and in this case also considered the latter to be a glucoside, whereas the former was sugar-free. The crystalline compound he described as very unstable and deliquescent; as this is not true of the pure pigment his crystals must have contained impurities—for it he gave the formula $C_{18}H_{26}O_{13}$. To the amorphous substance he gave the formula $C_{24}H_{44}O_{20}$, and from it by hydrolysis obtained glucose; here again he does not appear to have examined the resulting non-glucoside pigment. Of the crystalline substance he obtained 10 grams, together with 15 grams of the amorphous compound, from some 28 kilograms of fresh petals, which would point to a slight preponderance only of the glucoside in the petals if no hydrolysis took place during its isolation.

Having thus overcome the experimental difficulties involved, and having for the first time obtained considerable quantities of an anthocyan in crystalline condition, it is to be regretted that Grafe drew such incorrect conclusions from his results. Doubtless he had in mind those of Heise and Glan, that both glucoside and non-glucoside pigments were present in the plants they examined, for, on finding that his amorphous product reduced

Fehling's solution, but that his crystalline substance did not, he concluded that the former only was a glucoside, and convinced himself of this by its hydrolysis whereby he obtained glucose. Recent work has proved that Grafe's amorphous product must have been an impure specimen of the glucoside containing reducing sugars, whereas the crystalline substance was the glucoside in a practically pure condition; the possibility that such glucosides when pure do not appreciably reduce Fehling's solution never appears to have occurred to Grafe, and as a result he never seems to have attempted to hydrolyse his crystalline pigments. He concluded that his work, together with that of Heise and Glan, proved the co-existence, in the cases examined, of glucoside and non-glucoside in these plants. This conclusion has, however, been proved erroneous by the work of Willstätter and Everest, who have shown that only the glucoside there exists, accompanied in a few instances by a small percentage of sugar-free pigments.

During the years covered by this series of papers by Grafe, a considerable amount of work had been published by botanists, dealing with the formation of the anthocyans in plants. Miss Wheldale, as the result of much botanical work, came to the conclusion that the anthocyans are derived from colourless or faintly coloured chromogens (probably flavone or xanthone derivatives) by oxidation, most probably as the result of the action of peroxidases. She considered that the chromogens were produced by hydrolysis of glucosides that existed in the plant, this reaction being reversible. An essential feature of her theory is that the oxidation of the chromogen, with production of anthocyan, can only take place after the hydrolysis of the glucoside. To represent these changes she proposed the following scheme:—

$$\text{Glucoside} + H_2O \rightleftarrows \text{Chromogen} + \text{sugar},$$

then, Oxidation of chromogen * → Anthocyan pigment.

As chemical evidence of the latter part of these changes, Nierenstein and Wheldale (Ber., 1911, 44, 3487) and Nierenstein (Ber., 1912, 45, 499) brought forward products obtained by the oxidation of quercetin and chrysin respectively with chromic acid, which they described as "Anthocyan-like" products. The reactions from which they drew this conclusion were, however, by no means sufficient to show that any relationship exists between these compounds and the anthocyans. In this connection it is necessary to mention the observation of Perkin (Chem. Soc. Trans., 1913, 650), that

* This oxidation may, or may not, be accompanied by polymerisation.

gossypetin by oxidation in alkaline solution yields a substance (gossypeton) which is coloured deep blue by alkalis and red by acids. He pointed out the bearing of this observation upon the theory of Miss Wheldale. The fact, however, that this pigment is somewhat stable to alkalis is not in agreement with the properties of such anthocyans as have as yet been investigated, and indeed Perkin expresses doubt as to its existence as such in the cotton flower itself.

Keeble, Armstrong, and Jones (Proc. Roy. Soc., B., 1912, 85, 215; B., 1913, 86, 308, and 318; B., 1913, 87, 113; and Keeble and Armstrong, Jour. Genetics, 1913, 2, 277) have published a number of interesting papers upon the formation of anthocyans, and the hypothesis which they support is very similar to that of Miss Wheldale, but they part company with that author in regard to the process necessary subsequent to hydrolysis of the glucosides, for they maintain that the oxidation must be preceded by reduction of the non-glucosidal flavone or flavonol derivative.

In these experiments Keeble, Armstrong, and Jones came very near to the discovery of the true relationship that exists between the anthocyans and the flavones, for, in the light of later work described below, it is obvious that by some misfortune their reductions were carried too far (cf. Everest, Proc. Royal Soc., 1914, B., 87, 449).

In 1913 Willstätter and Everest (Annalen, 401, 189) published an account of investigations upon the anthocyan pigments, and in particular of the pigment of the corn-flower, and in this communication—the first of a series by Willstätter and his collaborators—some important conclusions were arrived at. It was proved that the blue form of corn-flower pigment was a potassium salt, the free compound being violet in colour, whereas the red form was not this latter, as had always been assumed by previous workers, but an oxonium salt in which the pigment was combined with an equivalent of some mineral or plant acid. The anthocyans were found to be most stable when in the form of these oxonium salts. It was also definitely proved that the decolorisation in solution, so often mentioned by other workers, was not due to reduction.

Having obtained the corn-flower pigment pure and crystalline in the form of its chloride, they proved that it was a disaccharide, since on hydrolysis 2 molecules of glucose were split off from each molecule of pigment; the sugar-free pigment was obtained in a finely crystalline condition. Microphotographs of the crystals were given. The pure glucoside does not reduce Fehling's solution.

By careful oxidation of cyanidin with hydrogen peroxide, a yellow crystalline product was obtained which in its reactions closely resembled a flavonol colouring matter.

To prevent confusion these authors proposed the terms *anthocyanins* and *anthocyanidins* for the glucoside and non-glucoside pigments respectively, and in agreement with this assigned to the glucoside present in the corn-flower the name introduced by Fremy and Cloëz—*cyanin*, whereas to the sugar-free pigment obtained by hydrolysis of cyanin the name *cyanidin* was given.

Willstätter and Everest introduced a method whereby they were able to distinguish between glucoside pigments of the anthocyan series and the corresponding sugar-free pigments. This depends upon the difference that exists between these classes of pigment in their distribution between amyl alcohol and aqueous acid. It has been very carefully studied by Willstätter and his collaborators in the course of their later work, and by but very slight modification it has been possible to utilise it in many cases to determine, with very considerable certainty, whether a given anthocyan pigment is a mono- or disaccharide, or a sugar-free pigment; and indeed in certain instances (e.g. chrysanthemum pigments) to separate mixtures of mono-, di-, and non-glucosides by its means, and show clearly the presence of all three. There are, however, limitations to its use for these purposes, dependent upon circumstances that are dealt with below.

Under suitable conditions of acid concentration Willstätter and Everest used dilute sulphuric acid *ca.* N — 2N; whereas in later work Willstätter and Zollinger use 0·5 per cent. hydrochloric, or sulphuric acid. The disaccharide anthocyans (with few exceptions) are almost quantitatively retained by the aqueous layer—in the form of their oxonium salts—when a solution of the pigment in aqueous acid is shaken with amyl alcohol; the monosaccharide derivatives, however, pass partially into the amyl alcohol layer—the percentage of the total pigment taken up by the alcohol being to a certain extent characteristic of the individual pigment. This may be quantitatively removed again by repeated washing with dilute aqueous acid, whereas, when sugar-free pigments are subjected to this test, the amyl alcohol layer takes the pigments quantitatively from the aqueous layer, and they cannot be removed from the amyl alcohol by washing with aqueous acid.

Willstätter and Zollinger have given the name "Distribution Number" (Verteilungszahl) to the percentage of the total pigment present which is taken up into the amyl alcohol layer when the above

test is carried out under certain conditions. These numbers are of considerable use in characterising a pure pigment of this series.

For the purpose of estimating the "Distribution Number" of an anthocyan, 0·01 gr. of the pigment is dissolved in 50 c.c. of 0·5 per cent. hydrochloric acid. In the original description of this method (Annalen, 1916, 412, 208) this is erroneously stated as 0·05 per cent. HCl, but the various references in the context, p. 208 and p. 209, make it obvious that 0·5 per cent. is meant. It is stated also that a more dilute acid allows of some isomerisation, whilst in more concentrated acids the pigments are less soluble (hence the choice of 0·5 per cent.). The solution is shaken twice with amyl alcohol (free from pyridine), using 50 c.c. amyl alcohol for each shaking. The small quantity of acid that passes to the alcoholic layer is sufficient to prevent isomerisation of the pigment in that layer.

The amyl alcoholic extracts are then quantitatively estimated by comparison (colorimetrically) with standard solutions of the pure pigment in amyl alcohol—also containing a small quantity of acid to prevent isomerisation. As the anthocyan pigments are not very soluble either in aqueous acid or in amyl alcohol, it is necessary to work with dilute solutions so that both layers shall remain unsaturated.

By these means Willstätter and Zollinger have obtained the following values :—

Pigment.	Type.	Distribution Number (Mean).
Malvin chloride	Diglucoside	1·6
Cyanin ,,	,,	1·8
Salvinin ,,	,,	*ca.* 1—2
Keracyanin ,,	Rhamno-glucoside	6·8
Prunicyanin ,,	,, ,,	9·7
Ampelopsin ,,	Mono-glucoside	9·8
Oenin ,,	,, ,,	10·4
Myrtillin ,,	,, ,,	10·8
Salvianin ,,	? Complex anhydro-di-glucoside	*ca.* 50
Salvin ,,	? Anhydro-diglucoside	57
Cyanidin ,,	Non-glucoside	100·0
Oenidin ,,	,, ,,	100·0

At one time it appeared as if diglucoside anthocyans had a number *ca.* 1—2, the monoglucosides *ca.* 10—11, and the non-glucosides 100, but the above table shows that this does not hold good now that further pigments have been investigated.

The discovery by Willstätter and Zollinger that certain diglucoside anthocyans have distribution numbers of the same order as

those of the monoglucosides, prevents the full use of this test in the direction in which they were developing it—viz. to characterise the three types of anthocyan pigments: non-glucosides, mono-, and disaccharides. Indeed, except in such cases where it is known that disaccharide pigments which have numbers similar to those of the monosaccharides are absent, it remains much in the position where Willstätter and Everest left it; i.e. that sugar-containing pigments either do not pass to the amyl alcohol layer, or, if they do so to some extent, they may be completely removed again by frequent shaking with fresh aqueous acid, whereas the sugar-free pigments pass quantitatively to the alcoholic layer and cannot be removed from it by such treatment.

With this method there are a few peculiarities that concern the sugars attached to the pigments, and which appear to show that these are of considerable importance in deciding the distribution number of these pigments.

Comparison of the values given in the table above, for disaccharide pigments, and of the products of their hydrolysis, shows that those which are rhamno-glucosides yield numbers that approximate to those of the monosaccharides.

Another very interesting case is that met with in the colouring matters of the salvia (scarlet). Here the flower pigment "Salvianin" appears to be rather more complex than most anthocyans (in this it resembles delphinin) in that on hydrolysis it yields pelargonidin, 2 molecules of glucose, and also malonic acid (proportion not yet determined), but by partial hydrolysis a compound "Salvin" is obtainable which appears to have the formula $C_{27}H_{26}O_{13}$, i.e. that of a pelargonidin diglucoside less 2 molecules of water, whilst a third pigment "Salvinin"—a true diglucoside of *pelargonidin*—is also obtained by partial hydrolysis of the original salvianin. Now, whilst salvinin, which is isomeric with pelargonin, behaves as a normal disaccharide anthocyan, i.e. gives a low distribution number, both salvianin—the original flower pigment—and salvin give extraordinarily high numbers, the former well over fifty, the latter almost exactly fifty. Willstätter ascribes these abnormal numbers to the diminution in the number of OH groups present in the sugar molecules attached to the pigment as is indicated by analysis, and by peculiarities observed during the carrying out of quantitative hydrolyses of these pigments.

By means of the test described above it has been shown that in almost every case investigated the anthocyan pigments are present in plants solely as glucosides; in a few instances, however, sugar-free

pigments appear to be present to a small extent also. Thus in black grapes (North Italian or hot-house grown) Willstätter and Zollinger (Annalen, 1916, 412, 206) found that the sugar-free pigment, *oenidin*, was present, but to the extent only of a few per cent. of the total pigment. In this respect a very interesting exception was met with by them in specimens of "Black Alicante" grapes, which were gathered at the Kgl. Gärtner-lehranstalt, Berlin-Dahlem, towards the end of November, and which had light brown-violet berries; in these they found (by colorimetric estimation) as much as 12 per cent. of the colour present as the non-glucoside pigment.

In 1914 Miss Wheldale (Biochem. Jour., 1914, 8, 204) published further work from which she concluded that the fact that she failed to obtain a crystalline pigment, and that her product had no melting-point, was evidence of the high molecular weights of the anthocyan pigments. By comparison with the case of cyanidin chloride, the melting-point evidence collapses at once, and it appears as though the non-crystalline condition of her pigment was either due to the presence of a small quantity of impurity, or that she did not ascertain the conditions for its necessary crystallisation.

That luteolin and morin give red pigments on reduction in acid alcoholic solution by means of sodium amalgam has been known for many years (cf. Rüpe, "Die Chemie der natürlichen Farbstoffe," vol. i., pp. 77 and 85). Watson and Sen (Chem. Soc. Trans., 1914, 389) obtained a red pigment from quercetin in like manner, whilst R. Combes (Comptes rend., 1913, 1002) produced a red pigment, identical with that which he had obtained from the red leaves of *Ampelopsis hederacea*, by reducing in the same way the yellow pigment obtained from the green leaves of the same plant. A further paper of Combes (Comptes rend., 1913, 1454) described the reverse change, viz. from red to yellow by means of oxidation with hydrogen peroxide. In each case he obtained crystalline compounds and compared their melting-points; he did not, however, give analyses, nor state whether he worked with glucosides or not.

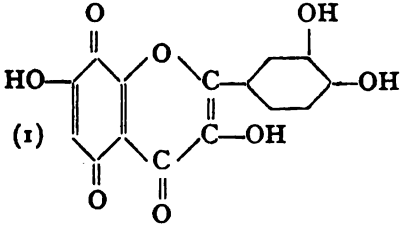
That a series of red pigments whose properties coincide in every way with those of the anthocyanidins may be produced by reduction of the flavonol derivatives by various methods, the best of which appears to be treatment of the pigment dissolved in a mixture of five volumes absolute alcohol and one volume concentrated hydrochloric acid, with magnesium, has been confirmed by Everest (Proc. Roy. Soc., 1914, B., 87, 444), who, moreover, in the same paper described the production, by the same means, of anthocyanins from the glucoside flavonol derivatives present in various flowers, thus showing

the direct formation of red glucoside pigments from the yellow flavonol glucosides without intermediate hydrolysis. This important observation makes the hypothesis of Miss Wheldale and others, in which hydrolysis of the flavonol glucoside is an essential factor, unnecessary, and moreover shows that reduction, not oxidation, is necessary for the passage from flavonol to anthocyan.

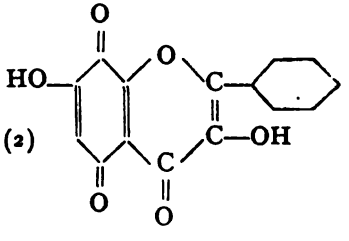
The results obtained, coupled with those of Willstätter and Everest in their investigation of the corn-flower pigment, led Everest to suggest a scheme to represent the passage from a typical flavonol to the corresponding anthocyan, and to put forward a structural formula for the anthocyans (see below). The correctness of these has been confirmed by the more recent work upon the natural pigments carried out by Willstätter and his collaborators.

Structure and Relationship to the Flavonols.

The first attempt to ascribe structural formulæ to the anthocyans was made by Nierenstein and Wheldale (Ber., 1911, 44, 3487), who, to produce chemical evidence in favour of Wheldale's theory of the formation of anthocyans from yellow sap pigments—flavone derivatives—prepared an oxidation product of quercetin. Subsequently Nierenstein (Ber., 1912, 45, 499) obtained a product in like manner from chrysin. They described these substances as anthocyan-like, though they stated that further investigation would be required to show whether they had really produced a true anthocyan. They represented the product obtained from quercetin (called *querceton*) by the formula (1), that from chrysin (*chryson*) by (2). In this connection cf. gossypeton (A. G. Perkin, Chem. Soc. Trans., 1913, 658).



(1)

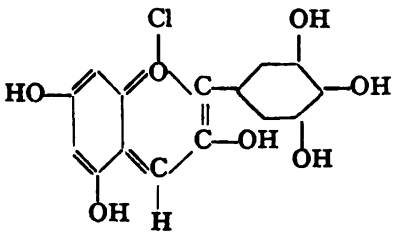


(2)

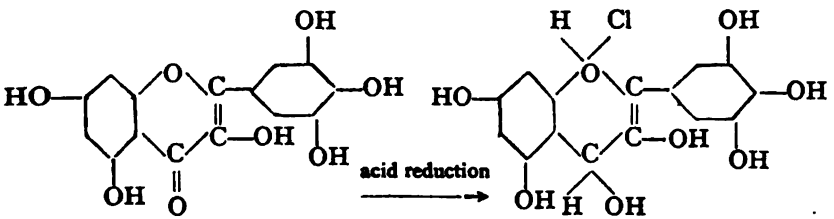
Investigations have since shown that these substances are not similar, either in properties or structure, to any of the anthocyans that have been investigated.

In 1914 (Proc. Royal Soc., 1914, B., 87, 449) the structural formula now generally accepted for the anthocyans was suggested

by Everest, who moreover cleared away some of the misconceptions that had been produced by botanical workers, and pointed out the relationship that exists between the yellow flavonol sap pigments and the anthocyans). He formulated a typical anthocyan thus :—

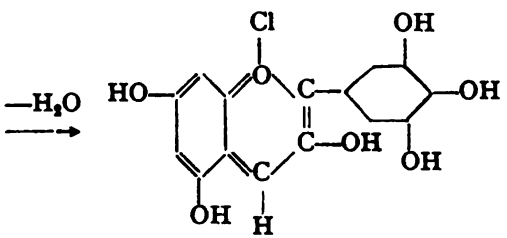


and considered the following scheme to represent the passage from a flavonol pigment (1) to one of the anthocyan series (3) :—



(1) Flavonol derivative.

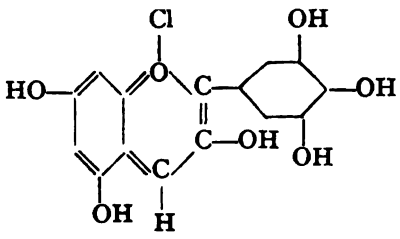
(2) Colourless, or faintly coloured intermediate product.



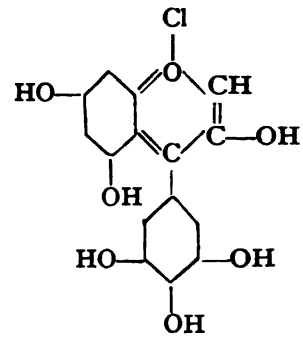
(3) Typical anthocyan.

Concurrently with Everest's investigations Willstätter was proceeding with the examination of these natural pigments, and as a result eventually to the same conclusions regarding their structure as Everest. Willstätter was unable to obtain from the examination of these natural products any distinction between the two following structures which seemed possible from the evidence he

had obtained by means of analyses and of their decomposition with alkalis, viz. :—



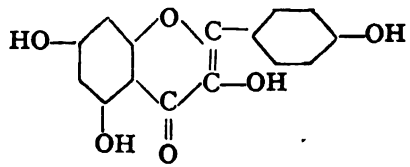
and



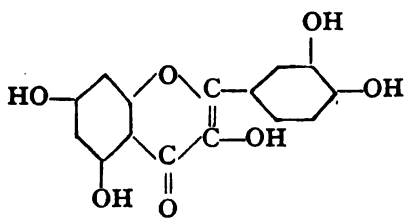
Willstätter was, however, able to show that pelargonidin, cyanidin, and delphinidin, three pigments of this series, were oxonium salts of the bases $C_{15}H_{10}O_5$, $C_{15}H_{10}O_6$, and $C_{15}H_{10}O_7$, and that by heating with concentrated caustic potash they all yielded phloroglucinol, and in addition to this, gave respectively *p*-oxybenzoic acid, protocatechuic acid, and gallic acid. In each case one OH group present in the anthocyan is unaccounted for by these decomposition products.

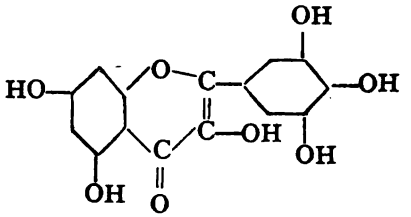
When this evidence is compared with the result of the alkali decomposition of the flavonol pigments kaempferol (1), quercetin (2), and myricetin (3), all of which yield phloroglucinol together with *p*-oxybenzoic acid, protocatechuic acid and gallic acid respectively—

(1)

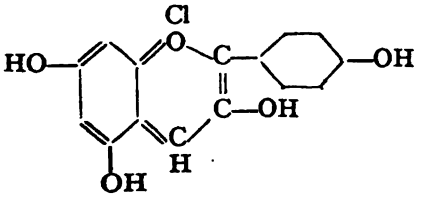


(2)

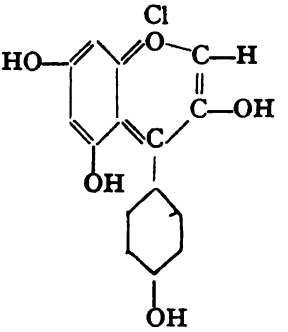


(3) 

and notice is taken of the fact that in each of these cases there is unaccounted for one OH group during decomposition, the evidence in favour of one or other of the following formulæ for pelargonidin chloride, though very strong, does not enable a decision to be made between them—

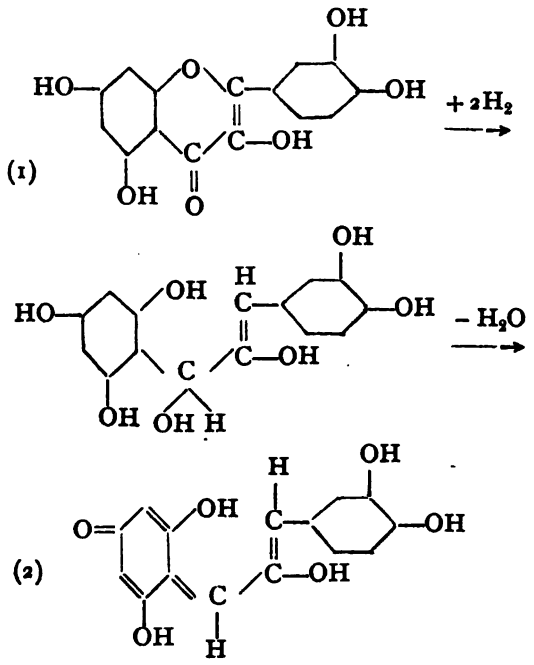


and



Willstätter was of the opinion that if the first formula was correct, then anthocyans should be formed by acid reduction of flavonols, and that the scheme put forward by Everest should represent this change. The first attempt of Willstätter and Mallison to carry out a synthetic preparation in this way led them, however, to the conclusion (Sitzber. d. Kgl. Preuss. Akad. d. Wiss., 1914, 402) that the red products obtained by Everest were not anthocyans. Further work (Everest, Proc. Roy. Soc., 1914, B., 88, 326; Willstätter and Mallison, Sitzber. d. Kgl. Preuss. Akad. d. Wiss., 1914, 769), carried out with a view to explaining the discrepancies thus arising, showed that under the conditions used by Everest anthocyans were really produced. Willstätter and Mallison prepared pure cyanidin chloride from quercetin, and proved it to be identical with the natural pigment, and as quercetin had previously been synthetically prepared by v. Kostanecki (Ber., 1904, 37, 1402), it completed the first synthetic production of an anthocyan pigment. On the other hand, it would appear that in their previous attempts Willstätter and Mallison had worked at much lower temperatures, under which

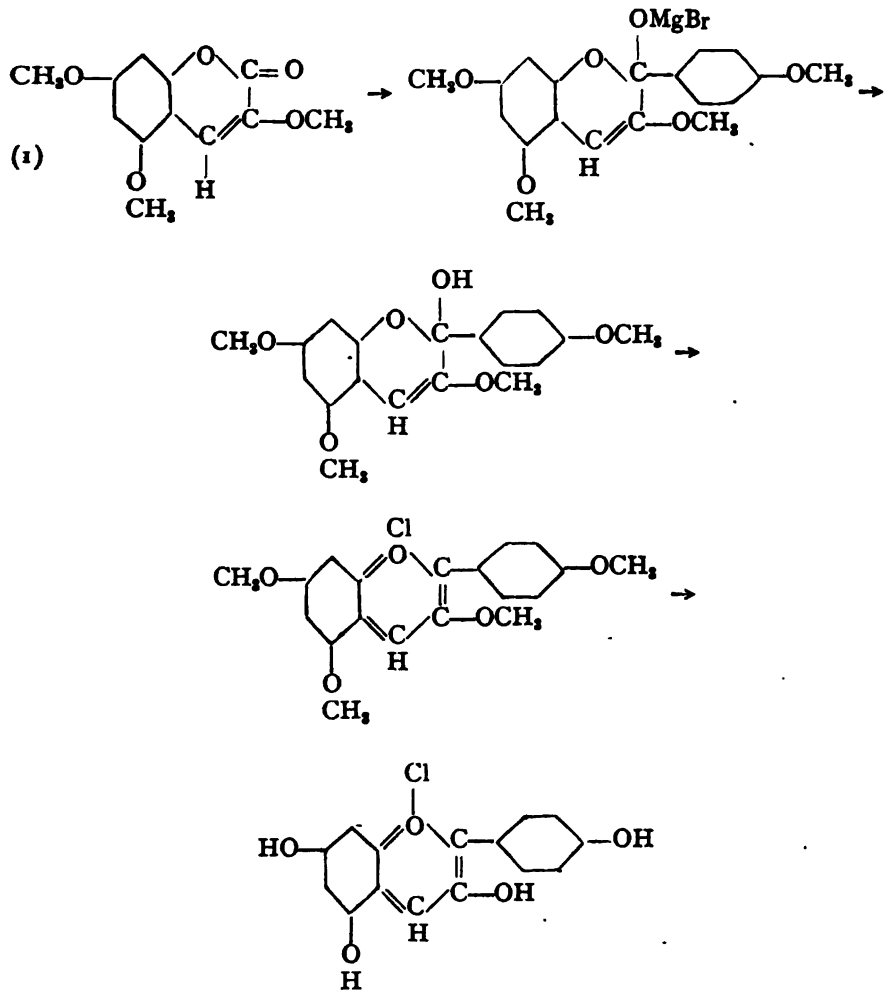
conditions the reaction proceeds differently, producing an unstable red compound to which they give the name *allocyanidin*, and ascribe the formula (2). They represent its production from quercetin (1) thus:—



Even at higher temperatures the change is said to proceed to some extent in this way, which, it will be noticed, assumes the opening of the pyrone ring during the reduction process.

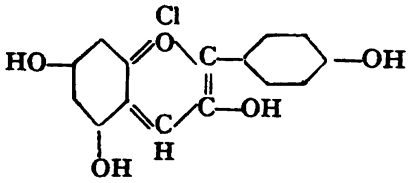
The structural formulæ thus established for the anthocyans is further confirmed by the work of Willstätter and Zechmeister (Sitzber. d. Kgl. Preuss. Akad. d. Wiss., 1914, 886), whereby *pelargonidin*—the anthocyan of the scarlet *pelargonium zonale*—has been synthesised by means of quite a different series of reactions. They started out from tri-methoxy-coumarin (1), and by reacting upon this with Grignard's reagent (magnesium-anisyl-bromide) and treatment of the product with hydrochloric acid, obtained a tetramethyl-ether, which on conversion to the free phenolic compound yielded an oxonium salt that proved to be identical with pelargonidin chloride, this being proved by means of analysis, solubilities, qualitative reactions, crystalline form, and absorption spectra. The stages of this synthesis may be represented thus:—

(1)

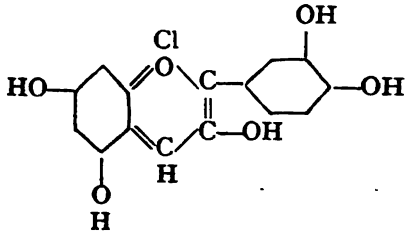


The further work of Willstätter and his collaborators on the natural pigments has very rapidly extended our knowledge of this series, and as a result, the constitution of quite a number of the members of this group is now clear. It is very interesting to notice that as yet no anthocyan corresponding to the naturally occurring flavones has been described, all those as yet investigated being derivatives of flavonol, and moreover that the anthocyanidins *pelargonidin* (2), *cyanidin* (3), and *delphinidin* (4)—

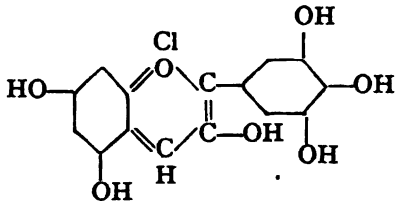
(2)



(3)



(4)



form the basis of all the other pigments of the series so far investigated. Sometimes difference in the position of attachment of the sugar residue, in other cases different sugars, give rise to different anthocyanins from the same sugar-free anthocyanidin, whilst methylation of one or other of the OH groups, or of more than one such group, produces new sugar-free pigments, which, like the parent substances, occur in a variety of different glucosides (anthocyanins).

That yellow sap pigments occur in flowers which contain anthocyans has been mentioned above, and this has given rise to a fairly general feeling among investigators that the latter are derived in nature from flavonol derivatives which are first produced by the plants, and not by direct synthesis. This view has received a certain amount of additional support from the chemical evidence obtained in a recent investigation by Everest (Proc. Royal Soc., 1918, B.), who isolated violanin—a delphinidin glucoside—from the flowers of purple-black violas, and showed that, unless gossypetin was present, the petals also contained a glucoside of the flavonol derivative myricetin, which latter (myricetin) can yield delphinidin by reduction.

Tinctorial Properties.

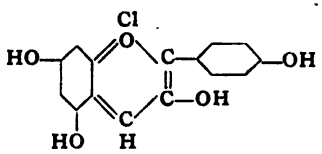
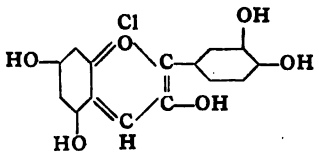
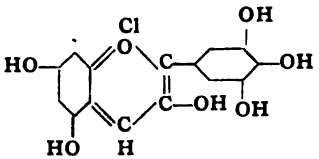
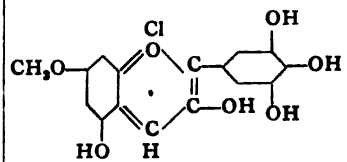
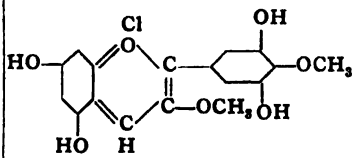
Though there are but few data available concerning the tinctorial properties of the anthocyan pigments, there can be little doubt that they are capable of acting as mordant colours, and it is interesting to find that, more than fifty years ago, the pigment of the black hollyhock was used in Germany—particularly in Bavaria—both for dyeing and printing. It is stated that the Bavarian Government encouraged the investigation of the chemical nature of this colouring matter, and that the work of Buchner, Elsner, and Kopp was the result (Bull. de la Soc. d'encouragement, 1860, 332; Polyt. Zentr., 1860, 1540). It was observed that an aqueous extract of the black flowers dyed cotton mordanted with iron blue-black shades; the same material mordanted with alum gave violet-blue, whilst with a tin mordant a blue-violet colour resulted. According to Kopp, these colours were more fast to light and air than the colours produced from logwood, but they gradually lose their intensity with age, and are not fast to soap. Recent work has shown that though the natural pigments of this series which are capable of giving dyeings are fast to light, they are all very fugitive to reagents (Willstätter and Mallison, Annalen, 1915, 408, 29).

The colours are taken up well by the fibre, it being stated that—excepting in the case of pelargonidin—the bath is exhausted even at low temperatures. The colours are strong—even ¼ per cent. dyeings being satisfactory—and the tones good though somewhat dull. The best dyeings are given with tin mordant on wool, or on tannined cotton, though in some cases the colours are taken up direct by unmordanted wool.

In regard to their dyeing properties the glucosides of the series react very similarly to the sugar-free pigments, and in this Willstätter and Mallison see evidence that the sugar groupings are not attached to the OH groups of the hydroxy-phenyl ring.

The dyeing properties of some of these pigments are collected together in the table on the next page.

For comparative purposes a bath was made up thus: 0·0025 gr. of the pigment was dissolved in a mixture of 10 c.c. alcohol and 40 c.c. water, the solution being made acid with 5 drops of 10 per cent. sulphuric acid (acetic acid is not used as it is not capable of preventing isomerisation—with formation of the pseudo base—nor the hydrolytic dissociation of the colour salt). To this bath 1 gr. of wool, or cotton, is added and left therein for one hour at a temperature of about 25° C.

Structure.	Pigment.	Wool.		Tannined Cotton.
		No Mordant.	Tin Mordant.	
	Pelargonidin.	Does not dye.	Purple-red.	Red, with bluish tinge.
	Cyanidin.	Fine rose.	Blue-violet.	Violet.
	Delphinidin.	Violet.	Blue, with violet tinge.	Blue-violet.
	Myrtillidin.	—	Violet-blue.	Violet.
	Oenidin.	—	Blue-violet.	Violet.

The dyeings thus produced are fast to light, but not to soap or water. Heating with water causes decolorisation, doubtless due to isomerisation with formation of the pseudo base, as is the case with dilute aqueous solutions of these pigments. Treatment of the dyeings with ammonia causes them to become blue, whereas mineral acids change them to red.

From the above data it will be observed that passing from pelargonidin → cyanidin → delphinidin, i.e. by the substitution of addi-

tional OH groups in the hydroxy-phenyl residue, the colour of the dyeings becomes bluer.

In order to appreciate the alteration in shade produced as the result of the structural change in the molecule on passing from flavonol to anthocyan, the following table is introduced:—

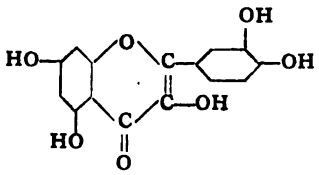
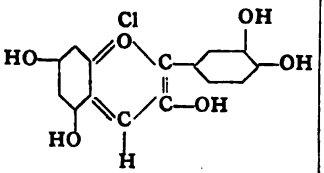
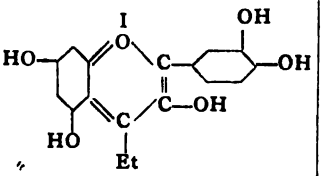
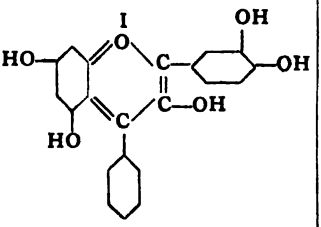
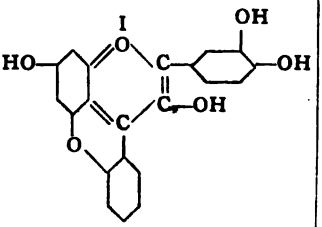
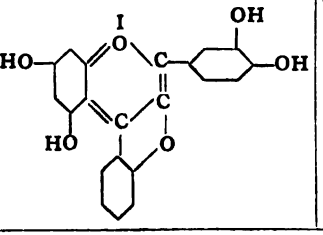
Flavonol.*	On Wool (Tin).	Anthocyan.†	On Wool (Tin).
Kaempferol . .	Lemon-yellow.	Pelargonidin .	Purple-red.
Quercetin . .	Strong orange.	Cyanidin .	Violet.
Myricetin . .	Strong orange-red.	Delphinidin .	Blue-violet.

It should further be noted that the great increase of the basicity of the oxygen atom of the pyrone ring that occurs in passing from flavonol to anthocyan is presumably the cause of the latter having the power of dyeing on tannin as well as on basic mordants.

The tinctorial properties of certain substitution products of the anthocyans have been studied by Watson (Chem. Soc. Trans., 1915, 1477). He prepared a series of compounds—by the interaction of Grignard reagents with flavonol derivatives—in which the H atom in the 4 position of the pyran ring is replaced by a variety of groups. The majority of his products are derivatives of cyanidin—obtained from quercetin—and the variation in the shade and properties of the dyeings produced by change in composition in this series of compounds is of considerable interest. In the table on the next page the most important points in this connection are brought together for comparison. The shades are those given on wool with various mordants.

A point of interest lies in the effect of methylation on the dyeing properties of these colours. It has been mentioned above, that as those anthocyanins of which the tinctorial properties were examined behaved similarly to the sugar-free pigments, Willstätter and Mallison concluded that the sugar groups in these compounds are not attached to the hydroxy-phenyl nucleus. Again, it should be possible, in certain cases, to deduce the position of the methyl groups by the effect of methylation on the tinctorial

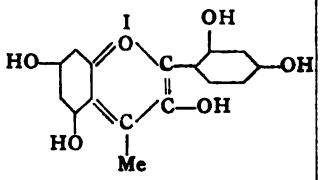
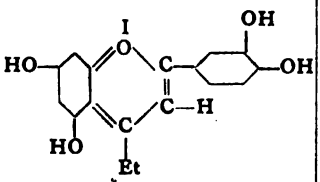
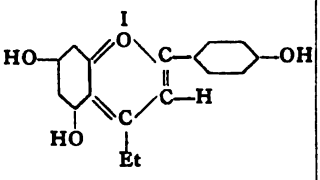
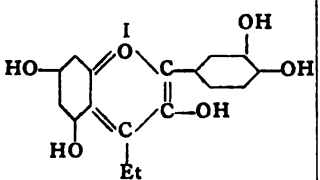
* A. G. Perkin, Chem. Soc. Trans., 1902, 589.
† Willstätter and Mallison, *loc. cit.*

Formula.	Alum.	Chrome.	Tin.	Iron.
(1) 	Brown-orange.	Red-brown.	Strong orange.	Olive-black.
(2) 	—	—	Blue-violet.	—
(3) 	Violet.	Violet.	Crimson.	—
(4) Tri-*ethyl* ether of (3).	Violet-blue.	Greenish-blue.	Violet.	Navy-blue.
(5) Tri-*methyl* ether of (3).	Terra-cotta.	Terra-cotta.	Terra-cotta.	Terra-cotta.
(6) 	—	—	—	—
(7) 	Greenish.	Green.	Dark blue.	Olive-green.
or 				

properties, and Watson refers to this in the case of two products obtained by him, and included in the above table. The great difference, both in shade and fastness to reagents, observed between the trimethyl ether prepared direct from quercetin-trimethyl ether by means of magnesium-ethyl iodide, and the triethyl ether obtained by partial de-ethylation (with aluminium chloride or sulphuric acid) of the product of the reaction of magnesium-ethyl iodide on quercetin-penta-ethyl ether is very interesting, and cannot be considered as being due to mere replacement of methyl by ethyl. It appears necessary, as Watson points out, to assume that it is caused by the attachment of alkyl to different OH groups in these two compounds (nos. 4 and 5 in above table).

In the natural anthocyan pigments methylation causes the shade of the dyeings on wool (tin mordant) to be shifted towards the red; thus Willstätter and Mallison record that delphinidin gives blue (with violet tinge), whilst its monomethyl ether (myrtillidin) gives violet-blue, and its dimethyl ether (oenidin) a blue-violet colour. Further, they state that these methyl derivatives have weaker dyeing properties than the free delphinidin, and, moreover, that in these cases the dye-bath is not exhausted. This latter effect is also noticed in the case of pelargonidin where there is only one OH group in the hydroxy-phenyl residue.

Everest has pointed out (*loc. cit.*) that as flavone derivatives (as distinct from flavonols) are fairly widely distributed in the plant world, and that flavonols also occur in which the OH groups in the oxy-phenyl nucleus are in the meta-position to one another, e.g. morin, and that as these, on acid reduction, yield red pigments resembling known anthocyans, it is probable that further investigation may lead to the isolation of natural anthocyans related to them in the same way that the known pigments of the series are to quercetin, etc. Up to the present no such bodies have been discovered, but, on the other hand, Watson has prepared (*loc. cit.*) a small number of products that are related to them in just the same way as his other compounds are related to the known anthocyans. His starting-points were morin, luteolin, and apigenin, from which, by the use of methyl- or ethyl-magnesium iodide, he obtained compounds represented by the formulæ (1), (2), and (3) respectively. The results of his examination of their dyeing properties are recorded beside their formulæ, and those of the corresponding derivative of cyanidin (4) added for comparison.

Formula.	Al.	Cr.	Sn.	Fe.
(1) 	—	Maroon.	Pink.	Salmon colour.
(2) 	Mauve.	Blue-black.	Maroon.	Blue-black.
(3) 	Brownish-orange.	Brownish-orange.	Orange.	Brownish-orange.
(4) 	Violet.	Violet.	Crimson.	—

The use of anthocyanin pigments as indicators has been suggested by various authors, e.g. Watson (Amer. J. Pharm., 1913, 85, 246), extract of blueberry pigment; Walbum (Biochem. Zeit., 1913, 48, 291), red cabbage pigment; but it should be noted that the colour change of many of these pigments, e.g. cyanin, is very seriously affected by neutral salts if present in any considerable quantity.

The Natural Pigments.

As previously noted, it is an interesting fact that but very few fundamental compounds form the basis of the comparatively large number of anthocyan pigments that have now been examined. Thus far, all the known colouring matters of this series are derived from pelargonidin, cyanidin, or delphinidin, though from

the most recent investigations there appears reason to hope that pigments of different origin may be isolated as the result of further work.

It is a curious coincidence that, before the investigation by Willstätter and Everest of cyanin and cyanidin was completed, it had been decided by them, as the result of preliminary experiments carried out in connection with the corn-flower work, that the pigments of the scarlet pelargonium and the wild larkspur (*Delphinium consolida*, L.) should be examined next. Work had indeed been commenced on them, and thus the three above-mentioned fundamental pigments were the first to be investigated by Willstätter and his collaborators, to whom we owe most of our present knowledge of these colouring matters.

The experimental difficulties to be overcome in the investigation of these pigments were very great until Willstätter and Everest, in their work on the corn-flower pigment, made clear the essential conditions, and further, introduced a rapid test that would distinguish glucoside from non-glucoside pigments.

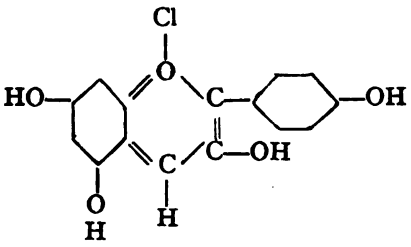
All the anthocyan colouring matters occur in plants in the form of glucosides, for the available evidence points to their being in nearly every case entirely in that condition. But a few instances have been definitely established in which a small percentage of sugar-free pigment accompanies the glucoside, and in only one exceptional case a considerable proportion of the total colour present was non-glucosidal.

The pigments, at present examined, occur in nature as mono- or diglucosides, and the sugars that have been obtained by their hydrolysis are glucose, galactose, and rhamnose; by far the largest portion of the pigments being in combination with glucose only, a smaller number are rhamno-glucosides, whereas, as yet, galactose has only been isolated from one colouring matter of the series.

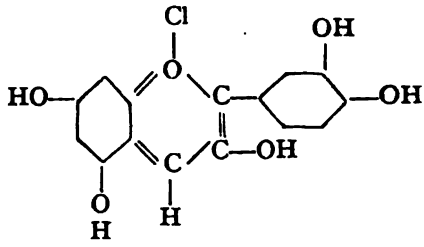
There are two very interesting abnormal cases of pigments (delphinin and salvianin) in which the natural colouring matter is not merely a complex containing the anthocyanidin combined with the sugar residues, but also with acid components. Thus delphinin, on hydrolysis, yields delphinidin, glucose, and *p*-oxybenzoic acid, whereas the pigment salvianin gives pelargonidin, glucose, and malonic acid. There is a further point of interest attached to the latter pigment, in that it does not appear to have the two molecules of glucose that it contains present as such, but in a derived form of the composition $C_6H_{10}O_6$, which is transformed into glucose on hydrolysis.

The three fundamental compounds forming the base of all the anthocyanins to be described below differ from one another only in the number of OH groups present in the molecule.

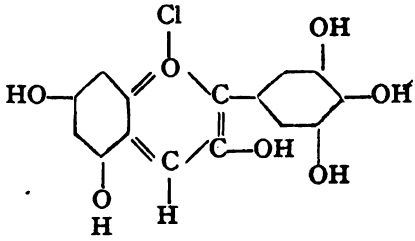
Pelargonidin, cyanidin, and delphinidin have been shown to have the structures represented by the formulæ (1), (2), and (3) respectively:—



(1)



(2)



(3)

and hence are

3 : 5 : 7 : trihydroxy-2-p-hydroxyphenyl-1 : 4 : benzopyranol anhydrochloride,

3 : 5 : 7 : trihydroxy-2 : mp-dihydroxyphenyl-1 : 4-benzopyranol anhydrochloride, and

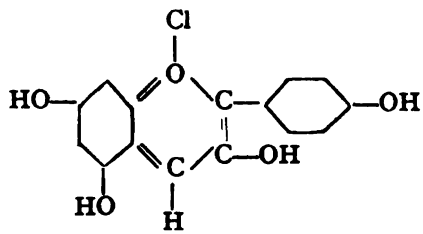
3 : 5 : 7 : trihydroxy-2 : mmp-trihydroxyphenyl-1 : 4-benzopyranol anhydrochloride.

Pelargonidin and its Derivatives.

Pelargonidin occurs in the form of glucosides in various flowers. It was first isolated from the scarlet *Pelargonium zonale* (Meteor)—hence its name; more recently also from the purple-red summer aster (*Callistephus chinensis*, Nees, syn. *Aster chinensis*, L.), the scarlet salvia (*Salvia coccinea*, L., and *Salvia splendens*, Sello.), and the rose-coloured corn-flower; whilst Willstätter and Bolton (Annalen, 1916, 412, 136), as the result of qualitative tests, conclude that the scarlet-red gladiolas also owe their colour to a pelargonidin deriva-

tive, and that traces are present in other gladiolas and in *Zinnia elegans* (Jacq.), of which the chief pigments are derivatives of cyanidin. Pelargonidin has also been prepared synthetically by Willstätter and Zechmeister, by the demethylation of the product obtained by the reaction of anisyl magnesium bromide on 3 : 5 : 7 : trimethox-coumarin (Sitzber. d. K. Preuss. Akad. d. Wiss., 1914, 886).

Pelargonidin forms a crystalline chloride which has the composition $C_{15}H_{11}O_5Cl$, and the structure—



This yields a hydrate $C_{15}H_{11}O_5Cl$, H_2O, which does not lose its water of crystallisation on drying in air, vacuum exiccator, or even in high vacuum at 50° C., but does so completely in high vacuum at 105° C. By treatment with hot water, preferably in presence of a trace of sodium bicarbonate, the chloride yields a pseudo-base which crystallises in colourless four-sided prisms; this product when dry has the composition $C_{15}H_{12}O_6$.

Pelargonidin chloride is readily prepared from any of its naturally occurring glucosides by hydrolysis with hydrochloric acid. This change takes place slowly in the cold if concentrated acid is used, but for the preparation of pelargonidin the glucoside is preferably boiled for three minutes with 20 per cent. hydrochloric acid (·2 gr. glucoside with 15 c.c. acid), the resulting product cooled to 65° C. (if further cooled the substance is contaminated by a by-product mentioned below), the crystalline chloride filtered off, washed with cold 20 per cent. hydrochloric acid and dried.

In this process it has been observed that whilst the pelargonidin chloride separates in brown-yellow leaflets, there is always some 5 per cent. of another product present in the reaction mixture, and this separates in needles. This product closely resembles pelargonidin, both in properties and composition, and can be prepared from it by the action of concentrated hydrochloric acid, but the reverse change has not yet been accomplished. It follows from this that long boiling in the preparation of pelargonidin from its glucosides is disadvantageous.

Pelargonidin chloride crystallises in three forms which are described by Willstätter and Bolton (Annalen, 1915, 408, 42) thus:—

(i) Long, not quite rectangular, red tablets—somewhat resembling crystals of xanthophyll.

(ii) Short red-brown, usually straight cut, four-sided prisms. These separate from hot dilute acid.

(iii) Sharply formed swallow-tail twin crystals, in form resembling carotin, but yellow-brown by transmitted light when viewed under the microscope. These are obtained by precipitation with concentrated hydrochloric acid.

Pelargonidin chloride is much more soluble in acids than is the cyanidin salt, being described as difficultly soluble in cold dilute hydrochloric or sulphuric acid, though fairly easily soluble when the acids are warm, forming solutions which are orange-red; from the solution in sulphuric acid the sulphate crystallises in needles on cooling. In methyl or ethyl alcohol the chloride is very easily soluble, yielding solutions that have a violet tinge, but show no fluorescence (cf. pelargonin); these solutions are not precipitated by the addition of water (cf. cyanidin). An aqueous acid solution of the chloride when shaken with amyl alcohol gives up all the pigment to the alcoholic layer, and if the red alcoholic solution thus produced is shaken with an aqueous solution of an alkali acetate it becomes violet, whereas if shaken with aqueous sodium carbonate, the colour turns to a fine pure blue and passes completely to the aqueous layer. These changes are the same as those observed with cyanidin chloride.

With reagents, the following are the most important reactions. Lead acetate, when added to an alcoholic solution, produces a blue precipitate; ferric chloride to an aqueous solution gives no characteristic coloration, and to an alcoholic solution only a brown-red tint (difference from cyanidin); Fehling's solution is noticeably reduced if warm.

When heated in a melting-point tube, pelargonidin chloride becomes darker, but does not melt below 350° C.

The chloride dissolves in water without separation of violet flocks (cf. cyanidin), forming a red solution which on warming (in the cold, if very dilute) becomes colourless as a result of the formation of the pseudo-base; if warmed with acids the colour is regained. The distribution number with respect to amyl alcohol is normal for a non-glucoside anthocyan = 100.

Willstätter and Bolton (*loc. cit.*) state that the absorption spectrum of this salt consists of two bands, one covering the spectrum from

yellow to blue, and another in the violet; both have edges that are badly defined. Thus far the presence of a band in the violet has not been observed in any other anthocyan, but they propose to reinvestigate this point photographically. Measurements given are:—

Thickness of solution:	2·5 mm.	5 mm.	10 mm.
Band I. . .	579...569—491..483	588..576—471.	586..583—
Band II. . .	448..442	448—	—

The action of caustic potash upon pelargonidin chloride has been studied, and it has been found that whilst 60 per cent. KOH, even at temperatures not above 100° C., yielded the phenolic decomposition product—phloroglucinol—it required much more concentrated caustic potash and higher temperatures to allow of the isolation of the acid decomposition product (*p*-hydroxy-benzoic acid). Thus 0·5 gr. of pelargonidin chloride were heated with 10 gr. KOH and 3 gr. water to 220° C., for two to three minutes; the product, after acidification, was extracted with ether and the ethereal extract shaken with sodium bicarbonate which leaves phloroglucinol in the ether from which it was isolated and identified; the aqueous layer yielded *p*-hydroxy-benzoic acid and a trace of protocatechuic acid. This production of protocatechuic acid resembles its formation from apigenin (Perkin, Chem. Soc. Trans., 1897, 805).

The ψ Base, $C_{15}H_{12}O_6$.—When pelargonidin chloride is heated with water (0·5 gr. with 600 c.c.) a pseudo-base is formed. The chloride dissolves, then the solution becomes decolorised — the addition of a small quantity of bicarbonate of soda (0·13 gr.) facilitates complete decolorisation—and the base can be obtained from this solution by the addition of salt followed by the extraction of the product with ether. It is finally recrystallised from water at 50° C., and in this way the base separates in the form of four-sided prisms.

The base is very easily soluble in alcohol, ether, or hot water, less soluble in cold water, and insoluble in benzol. If a cold aqueous solution be acidified with hydrochloric acid it slowly deposits crystals of the chloride; if the solution is hot, the chloride is very rapidly formed. The base gives a bright yellow coloration on addition of sodium carbonate. No definite melting-point can be observed when the pure substance is heated, the crystals turn red, then very gradually soften till a dark violet oil is produced; melting not taking place below 350° C.

Derivatives of Pelargonidin.

1. Monosaccharides.

Callistephin.—Callistephin is one of the two pigments isolated by Willstätter and Burdick (Annalen, 1916, 412, 149) from the flowers of purple-red asters (*Callistephus chinensis*, Nees, syn. *Aster chinensis*, L.), in which it occurs together with a larger quantity of *asterin*, a monoglucoside of cyanidin. The petals contain about 7·4 per cent. of their dry weight of the mixed pigments.

Of the several methods used for the isolation of the mixed pigment (asterin and callistephin) from the flowers, it appears that the use of their lead salts produces the best results. Their value for this purpose was due to the discovery that glacial acetic acid dissolved the lead salts of the colouring matters but not those of the colourless impurities that accompanied them, and further, that by decomposition of the lead salts by propylalcoholic hydrochloric acid the colourless impurities remained insoluble whilst the alcohol retained the pigments in solution. Willstätter and Burdick used glacial acetic acid for the extraction of fresh or dried petals, but state that for the latter it is not so satisfactory, methyl alcohol containing a small percentage of hydrochloric acid being the best solvent. They proceeded in the following manner. The glacial acetic acid extract (8·9 lit. from 3·2 kg. petals) was precipitated, without addition of hydrochloric acid, by twice its volume of ether, and the product (65 gr. syrup, 10 per cent. pure) dissolved in 0·01 per cent. HCl (600 c.c.), filtered from insoluble residue, and the filtrate treated with a solution of lead acetate (12 gr. in 50 c.c. water) which completely precipitated the colouring matter. The product was collected, washed with 0·01 per cent. HCl, and treated whilst moist with glacial acetic acid (600 c.c.), filtered, and the filtrate diluted with twice its volume of ether, whereby the lead salts of the pigments were precipitated (14·7 gr.). When the product thus obtained was decomposed by treatment with propylalcohol (200 c.c.) containing 25 per cent. methyl alcoholic hydrochloric acid (20 c.c.), filtered, and the filtrate precipitated by addition of ether (600 c.c.), the anthocyan mixture was obtained 70 per cent. pure (6·5 gr.). On repetition of the process the chloride was obtained 85 per cent. pure (4 gr.), in which condition it was pure enough to yield a crystalline picrate, or for the purpose of separating callistephin from asterin. The product obtained as above was fractionated by solution in a mixture of methyl or ethyl alcohol and aqueous hydrochloric acid, allowing the alcohol to evaporate off slowly. From the earlier crops precipitated pure asterin was obtained, whereas from the

mother liquors callistephin was isolated by addition of alcohol, then ether, or if sufficient alcohol was already present, by ether only. The precipitate produced was recrystallised from a mixture of alcohol and aqueous hydrochloric acid from which it separated in fine orange-red needles.

Callistephin chloride, $C_{21}H_{21}O_{10}Cl$, crystallises in hair-fine, orange-red needles which in bulk form a bronze-coloured mass; they contain 2—2½ molecules of water of crystallisation, and are hence of the same composition as crystalline pelargonenin chloride.

It is easily soluble in water, giving a yellowish-red solution which on dilution becomes tinged with violet and slowly decolorises owing to pseudo-base formation. In cold or hot alcohol it is easily soluble, the solution being yellow-red, but showing no fluorescence; it gives a red solution in amyl alcohol. The salt is characterised by great solubility in aqueous acid, being very easily soluble in hydrochloric acid up to 7 per cent. and fairly so in 10 per cent.—solutions in higher per cent. HCl gelatinise on standing—and is easily soluble in 7 per cent. sulphuric acid.

Ferric chloride gives no colour reaction with callistephin chloride; with sodium carbonate, or caustic soda, an acid solution of the salt passes to red-violet or violet-red.

The distribution number of callistephin resembles that for other normal monoglucoside anthocyans, and hydrolysis of callistephin chloride yields *pelargonidin chloride* (1 mol.) and *glucose* (1 mol.).

Pelargonenin.—Pelargonenin results from the careful partial hydrolysis of pelargonin (Willstätter and Bolton, Annalen, 1916, 412, 133), and has not as yet been discovered to occur naturally. 7 gr. pelargonin chloride are dissolved in cold concentrated hydrochloric acid (250 c.c.), filtered through glass wool and the solution allowed to stand. The separation of scarlet-red flakes soon commences, and after eighteen hours these are filtered off (*ca.* 1·6 gr.); the filtrate after the addition of further acid (100 c.c.) is left for three days, by which time some further (2 gr.) brown-red product has separated, which, however, has to be purified from pelargonidin; the residual liquor contains pelargonidin. The crude product is best purified by dissolving in 0·05 per cent. HCl (1·3 gr. in 150 c.c.), shaking twice with amylalcohol (100 c.c. and 75 c.c. respectively)—this must be done rapidly to prevent precipitation of the pigment from the aqueous solution; after extraction and separation the amount of acid is increased to 2 per cent. HCl when the pigment separates in flakes. The product thus obtained is recrystallised from warm 2 per cent. HCl, when it is deposited in the form of fine scarlet-red needles.

Pelargonenin chloride thus prepared has the composition $C_{21}H_{21}O_{10}Cl \cdot 2H_2O$ (? $2\frac{1}{2}H_2O$), loses 1 molecule of water on drying in vacuum desiccator, and the remainder in high vacuum, yielding the anhydrous salt $C_{21}H_{21}O_{10}Cl$. On hydrolysis each molecule of pelargonenin chloride yields 1 molecule of *pelargonidin chloride* and 1 molecule of *glucose*.

The salt is very difficultly soluble in cold water, dilute hydrochloric acid, or dilute sulphuric acid, but is more soluble in warm acids; its solutions in aqueous hydrochloric acid are yellower than corresponding solutions of pelargonidin chloride, but less yellow than those of pelargonin chloride. It is easily soluble in methyl alcohol which contains hydrochloric acid, and fairly so in ethyl alcohol in presence of the same acid; such solutions are intermediate in colour between those of the chlorides of pelargonidin and pelargonin, but they show much stronger fluorescence than those of the latter.

Of the reactions recorded the following may be mentioned. An acid solution on addition of sodium carbonate becomes violet, passing then to violet-blue (pelargonidin gives blue), and the violet-blue is more stable than the blue given by pelargonidin; if the solution of pelargonenin be alcoholic, addition of alkali gives a pure blue colour. Lead acetate added to an alcoholic solution of the salt gives a blue precipitate. Picric acid slowly causes precipitation of a crystalline picrate (needles) when added to a solution just acid with hydrochloric acid; ferric chloride produces no colour reaction.

The differences between callistephin chloride and pelargonenin chloride are well shown by the following data given by Willstätter and Burdick :—

	Callistephin Chloride.	Pelargonenin Chloride.
Crystalline form . .	Orange-red hair-fine needles.	Scarlet-red needles.
Solubility in H_2O . .	Easily soluble.	Slightly soluble.
„ „ HCl . .	Very easily soluble.	Very difficultly soluble.
Colour of acid solution	Yellow-red in alcohol, *no* fluorescence.	Yellow-red with bluish tint, *strong* fluorescence in alcohol.
Reaction with soda .	Red-violet—violet-red.	Violet-blue.

Concerning the monoglucoside produced from salvinin (*loc. cit.*) in the same manner as pelargonenin is prepared from pelargonin, that is by partial hydrolysis, there is as yet but little known.

2. DISACCHARIDES.

Pelargonin.—This pigment, named by Willstätter and Bolton (Annalen, 1915, 408, 42) after the pelargonium from which it was isolated by them, was the first anthocyan to be obtained in a crystalline condition (A. B. Griffiths, Chem. News, 1903, 249; Ber., 36, 3959). Griffiths suggested for it the formula $C_{15}H_{10}O_6$, described a potassium salt and an acetyl derivative, and gave data concerning absorption spectrum and specific rotation, but his descriptions are very superficial, and in the light of more recent work these do not appear to be reliable. In 1905, H. Molisch (Bot. Ztg., 1905, 145) examined the pelargonium pigment from a botanical standpoint, and showed how readily this pigment could be obtained in a crystalline condition. A slightly modified form of his process forms a useful experiment for lecture demonstration. The work of Molisch caused Grafe to attempt the chemical investigation of the pelargonium pigment (Sitzber. d. K. K. A. Wiss., Wien, 1911, 765). He succeeded in obtaining the pigment in the crystalline condition by the use of glacial acetic acid as solvent, by preparation of the lead salt and liberating the free pigment from this, or by the dialysis of a solution of the pigment. Besides the crystalline product, he isolated a second substance which was amorphous in character, and employing 25 kg. of fresh petals he obtained 10 gr. of the crystalline pigment and 15 gr. of the amorphous substance. Grafe described the crystalline compound as very unstable and deliquescent, proposed for it the formula $C_{18}H_{26}O_{13}$, and considered that it was a tribasic acid having two hydroxy and two carbonyl groups within the molecule, and was a sugar-free compound. To the amorphous substance he gave the formula $C_{24}H_{44}O_{20}$, and showed it to be a glucoside as he obtained glucose from it by hydrolysis; he does not appear to have examined the resulting sugar-free compound. Grafe suggested that the two pigments obtained by him were related to each other, and might be formed according to the following scheme: $C_{24}H_{44}O_{20} + H_2O \rightarrow C_6H_{12}O_6 + (C_{18}H_{24}O_{15})$ (hypothetical product), then $(C_{18}H_{24}O_{15}) - 4H_2O + O_2 \rightarrow C_{18}H_{26}O_{13}$. Grafe described various reactions and also the decomposition products resulting from melting the pigments with caustic potash, but his results have not been confirmed by later work. Willstätter and Bolton (*loc. cit.*), who have thoroughly investigated the pigment of the pelargonium, state, in

regard to Grafe's results, that the anthocyan is quite a stable compound, gives no ferric chloride reaction, and with sodium carbonate yields a violet coloration. It contains neither carbonyl nor carboxyl groups, and does not yield protocatechuic acid nor catecol when decomposed by caustic potash.

According to Willstätter and Bolton, pelargonin is the only pigment present in the scarlet *Pelargonium zonale* (Meteor), in the petals of which it occurs to the extent of 6·6—7·1 per cent. of their dry weight. These authors also show that it occurs in other flowers—e.g. pink corn-flower, cactus dahlia (Annalen, 1915, 408, 149).

For the preparation of the pure pigment, as chloride, Willstätter and Bolton extract the flowers either with glacial acetic acid or 96 per cent. alcohol—the latter gives more complete extraction and a purer product, and was the solvent used by Griffiths. Using acetic acid they proceeded thus: 3 kg. fresh petals were allowed to stand some time in 4 litres of glacial acetic acid, filtered, and, as the extraction was not complete even after long standing, the residue was re-extracted with a further 2 litres of acid and again filtered. The extracts were united and had a deep red colour and faint green fluorescence. To each 500 c.c. of the extract 50 c.c. of alcoholic hydrochloric acid (as low as 2 per cent. HCl may be used, but preferably, somewhat stronger, even to 20 per cent. HCl, as precipitation is then better), then 1 litre of ether was added which caused the precipitation of the pigment, this being complete in a few hours. A further 100—200 c.c. of ether added to the filtrate leaving to stand for a few days precipitated a further quantity of pigment. The major portion of the colouring matter was thus obtained, the first fraction being the purer; it was not found advantageous to work up the further filtrates. 570 gr. petals yielded 6·7 gr. of crude chloride (38·4 per cent. pure), i.e. 63 per cent. of the total pigment contained in the petals.

By using in place of acetic acid 96 per cent. alcohol the pigment was much more completely extracted from the petals, so much so, that a re-extraction was deemed to be unnecessary, the residue from the first extraction being merely washed on the filter with fresh alcohol, and a purer crude product was subsequently obtained. The alcoholic extract—and the petals lying therein—became decolorised after standing a few days, owing to pseudo-base formation, but the change had no detrimental effect on the preparation as the addition of a little hydrochloric acid, even cold, reproduced the colour, whereas if ether were added a violet precipitate of the colour base separated. For the preparation of pelargonin chloride

Willstätter and Bolton took 1 litre of the alcoholic extract and added 20 c.c. of alcoholic hydrochloric acid (20 per cent. HCl), followed by 2 litres of ether, whereby a carmine-red flocculent precipitate was thrown down. The precipitate filtered readily and the filtrate contained but traces of the colouring matter.

The crude chloride obtained by either of the above methods was purified by fractional precipitation from solution in methyl-alcoholic hydrochloric acid by ether, or better, by recrystallisation from methyl-alcoholic acid, or a mixture of methyl alcohol, water, and hydrochloric acid in the following way. The impure product was dissolved by boiling for a short time in 2 per cent. methyl-alcoholic hydrochloric acid, filtered warm, to remove insoluble impurities, and the filtrate mixed with $\frac{1}{4}$—$\frac{1}{2}$ of its volume of 10 per cent. aq. HCl. (In this solution the glucoside is not hydrolysed, even on long standing.) On cooling, fine long thin needles of the chloride separated, and after filtration a further almost equally pure crop was obtained by careful slow evaporation of the methyl alcohol from the mother liquor. The recrystallisation was repeated several times if the pigment was desired in a state of complete purity.

Pelargonin chloride has the composition $C_{27}H_{31}O_{15}Cl$, and forms a hydrate $C_{27}H_{31}O_{15}Cl$, $4H_2O$, which loses its water in a vacuum desiccator at room temperature, and crystallises in long thin red needles; the anhydrous salt softens at 175° C. and melts with decomposition at 180° C.

In cold dilute hydrochloric acid (1—2 per cent. HCl) the crystalline salt is difficultly, and in 5 per cent. HCl very difficultly soluble, but is easily soluble in these acids if hot, giving orange-red solutions; hydrolysis takes place, however, if the solutions in any but very weak acids are warmed.

In water the salt is appreciably soluble giving an orange-coloured solution, but the colour becomes violet as the result of hydrolytic dissociation, and then, even when cold, gradually becomes colourless owing to the formation of the pseudo-base. The alcoholic solutions are more stable; in cold methyl alcohol the salt is appreciably soluble, and readily soluble in the warm solvent from which it crystallises on cooling—the yellow-red solution has a characteristic greenish-yellow fluorescence; in ethyl alcohol the compound is less soluble, and if it be heated with a small quantity of this the normal chloride is converted into a basic salt.

In respect of its distribution between aqueous acid and amyl alcohol pelargonin behaves as a normal diglucoside. The hydrolysis of pelargonin yields either pelargonidin, the sugar-free pigment, if the

hydrolysis be carried to completion, or pelargonenin, an intermediate monoglucoside, if the hydrolysis be carried out carefully under prescribed conditions.

With reagents the following changes may be noted: lead acetate, sodium acetate, or calcium carbonate cause the precipitation of the violet colour base when added to a solution of the chloride; ferric chloride, or alum, produces no colour reaction; sodium carbonate gives a violet colour (cf. pelargonidin), which gradually changes to greenish-red then to yellow—sodium or ammonium hydrate gives the same reaction; in alcoholic solution the addition of sodium hydrate gives a fine blue colour, which passes to violet on dilution with water; sodium bisulphite forms a colourless easily soluble addition product; Fehling's solution, even warm, is only reduced to a very small extent.

Pelargonin chloride is optically active, and Willstätter and Bolton give the following values:—

$[\alpha]_D = -291°$, $[M]_D = -1837°$; & $[\alpha]_{614} = -180°$, $[M]_{614} = -1133°$.

The absorption spectrum has also been investigated by them, and is described as consisting of one broad band passing much less into the green than that of cyanin, ending very indistinctly at that end, whilst the violet region is darkened, particularly on the edge of the visible portion. They give the following data:—

1 mol. in 2500 litres	2·5 mm. layer.	536 . . 530 – 458 .
0·5 per cent. aq. HCl.	5·0 „ „	547 . 542 – 447 . .

Pelargonin basic chloride $(C_{27}H_{31}O_{15}Cl)_2 . (C_{27}H_{30}O_{15})$ is prepared by boiling 1 gr. pelargonin chloride with 250—300 c.c. of 96 per cent. alcohol for a few minutes. Some of the product remains undissolved, though converted into violet flakes, but from the orange-red filtrate crystals separate on cooling, which consist of small deep violet needles possessing metallic lustre. The crystals are of a hydrate $(C_{27}H_{31}O_{15}Cl)_2(C_{27}H_{30}O_{15}), 12H_2O$, which loses its water (not alcohol) of crystallisation in a vacuum desiccator, leaving the anhydrous compound consisting of 1 mol. base and 2 mols. chloride.

Pelargonin acetate $(C_{27}H_{31}O_{15})_2 . (C_{27}H_{30}O_{15} . C_2H_4O_2)$ is prepared by dissolving pelargonin base (see below) in boiling 90 per cent. acetic acid, and allowing the filtered solution to cool when the acetate separates in fine red needles. It also separates from a glacial acetic acid extract of pelargonium petals (in which pelargonin is probably present originally as tartrate). In a vacuum desiccator the crystals lose 9·33 per cent. of their weight, probably of acetic acid, and the dry product gives analytical figures which agree with the above

formula. Doubtless the crystalline substance obtained by Grafe consisted of this acetate in an impure state.

Pelargonin base, $C_{27}H_{30}O_{16}$.—This compound is prepared by treatment of the chloride with a small quantity of water, or by addition of sodium acetate to a weakly acid solution of the pigment. It has not been obtained crystalline, but for analysis was merely washed free of chloride by means of water. It is difficultly soluble in water, the solution becoming gradually decolorised owing to pseudo-base formation; in alcohol it is very difficultly soluble, whereas in alkalis it is readily soluble with the formation of an unstable violet solution.

Diglucosides of Pelargonidin obtained from the Flowers of the Scarlet-red Salvia (Salvia coccinea, L., *and S. splendens*, Sello).

SALVIANIN, SALVIN, and SALVININ (Willstätter and Bolton, Annalen, 1916, 412, 113).

Of these three compounds salvianin is the colouring matter that occurs in the flowers, salvin and salvinin being hydrolytic products obtained from it, which are diglucosides of pelargonidin.

Salvianin.—As this compound has not yet been obtained in a crystalline condition—despite the formation of a finely crystalline picrate—the data concerning it must be looked upon as somewhat incomplete and preliminary; Willstätter promises further investigation. (It should be noted, in this connection, that descriptions given by Willstätter and his collaborators in their later papers are not so complete as those of the earlier ones, this being due to the abnormal conditions under which the work was carried out.)

In *Salvia splendens* (dry petals) the pigment is present to the extent of about 6 per cent., and is not accompanied by any non-glucoside anthocyan. The crude colouring matter was obtained by Willstätter and Bolton, as acetate, by extracting the petals (fresh) with ten times their weight of glacial acetic acid for some days, and precipitating the extract thus obtained by means of ether—1 kg. of petals yields 20 gr. crude product. The substance thus obtained was purified by either of two methods, but in no case could the compound be obtained in a crystalline condition except in the form of the picrate. One method consisted in adding a saturated solution of picric acid to a solution of the crude acetate in 0·05 per cent. HCl, whereupon the picrate separated, and by treatment with methyl-alcoholic hydrochloric acid was converted into the chloride,

and this was purified by fractional precipitation from methyl-alcoholic hydrochloric acid by means of ether. The other, which is of interest in view of the fact that it takes advantage of the abnormal distribution number of this pigment, depended upon the fractional extraction of the pigment from its aqueous acid solution by means of amyl alcohol. This is tedious and requires large bulks of solvents for quite small quantities of pigment.

Salvianin chloride.—This as purified consists of a solidified oil of brownish-red colour with a metallic lustre. After drying in high vacuum analyses gave C = 54·12 per cent.; H = 4·64 per cent.; Cl = 4·40 per cent.; and hydrolysis showed that the compound yielded *pelargonidin chloride* ($C_{15}H_{11}O_5Cl \cdot H_2O$), 35·5 per cent. to 37·6 per cent.; *glucose*, 29·5 per cent. to 33·4 per cent.; and *malonic acid*, 24·6 per cent. to 26·7 per cent. It would appear therefore that salvianin is a complex body which yields malonic acid as well as glucose on hydrolysis, and hence resembles delphinin; moreover, salvianin is remarkable in that it seems very probable that the glucose molecules are not there as such, but in the form of a derivative containing a smaller number of OH groups and of the composition $C_6H_{10}O_5$. Polarimetric evidence points to this derived sugar being first liberated when salvianin is hydrolysed, this passing into glucose as the result of further hydrolysis. In addition to this peculiarity salvianin shows a very marked difference from all other known diglucosides, except salvin (see below), in respect of its distribution number. Of the other known disaccharides of the anthocyan series, only the rhamnoglucosides have a distribution number approaching that of the normal monoglucosides, viz. *ca.* 10, all the diglucosides having numbers about 1—2, but in the case of salvianin the number is as high as 50 (cf. salvin).

Salvianin chloride is about $\frac{2}{3}$ as intense a colouring matter as salvin chloride; it is very easily soluble in very dilute hydrochloric acid (0·5 per cent. HCl), and fairly so in stronger acid (100 c.c. of 4 per cent. HCl dissolves 0·13 gr. at 20° C.), and its solutions in aqueous acid are rather more red than those of pelargonin chloride, whilst those in alcohol are less so. The solid salt changes to an oil on the addition of water, but only forms a solution if little water is used, and on addition of more water the pigment is reprecipitated in the form of red flakes of a basic salt. With very much water a colourless solution of the pseudo-base is formed from which, on addition of acid, the colour is reproduced.

The salt is very readily soluble in ethyl or methyl alcohol if acid

be present, forming yellow-red solutions with fluorescence (not so strong as pelargonin); these on addition of alkali give a pure blue colour, whereas an aqueous acid solution of the pigment with caustic soda gives violet rapidly passing to yellow, with sodium carbonate a violet, and with sodium acetate a violet-red colour.

In the presence of hydrochloric acid salvianin is gradually converted into a second diglucoside of pelargonidin—salvin—which can be obtained in fine crystals, and further to a third—salvinin. Both of these products are best obtained by allowing a solution of purified salvianin in dilute hydrochloric acid to stand in a desiccator containing concentrated hydrochloric acid which is kept at 30 per cent. strength by addition of fresh concentrated acid from time to time. In this way oily drops are at first precipitated, followed by a second fraction in the form of deep red tablet-like prisms (salvin chloride), whilst the mother liquors contain salvinin chloride.

Salvin chloride.—For this compound Willstätter and Bolton tentatively suggest the formula $C_{27}H_{27}O_{12}Cl$ (i.e. pelargonin chloride $-2H_2O$), and state the following reasons for considering that salvianin is not merely an impure form of salvin: (1) salvin (crystalline) gives only an oily precipitate with picric acid, whereas salvianin (amorphous) yields a finely crystalline picrate; (2) under suitable conditions salvianin readily forms a basic salt, whereas salvin does not do so when similarly treated; (3) salvianin is more strongly fluorescent than salvin. It is unfortunate that as the chloride loses hydrochloric acid on complete drying, the analytical data have had to be calculated back to the chlorine-free base; when this is done, however, good agreement is obtained. Moreover, the formula, which requires the glucose to be present, as in the case of salvianin (see above), in a derived form having the composition $C_6H_{10}O_5$, is supported by the abnormal rotation observations which point to an intermediate sugar hydrolytic product being first produced which by further hydrolysis yields glucose, and also by the exceedingly high distribution number, which for this pigment is no less than 57.

The crystalline pigment is easily soluble in water without precipitation of a basic salt (cf. salvianin), forming an orange-red solution—very dilute aqueous solutions become decolorised owing to pseudo-base formation—and in dilute hydrochloric acid yields an orange-yellow liquid. It is very soluble in methyl or ethyl alcohol, and these solutions fluoresce, but less strongly than similar solutions of pelargonin or salvianin chlorides.

With reagents the following reactions are recorded: Aqueous, or aqueous acid solutions of salvin chloride on addition of sodium

acetate give a violet flocculent precipitate, whereas sodium carbonate produces a violet coloration, and caustic soda a violet colour that rapidly passes to yellow. Lead acetate produces a violet flocculent precipitate.

On complete hydrolysis salvin chloride yields *pelargonidin chloride* (1 mol.) and *glucose* (2 mols.).

Salvinin chloride, $C_{27}H_{31}O_{15}Cl$, which behaves in every way as a normal diglucoside anthocyan, and which is isomeric with pelargonin chloride, was obtained by Willstätter and Bolton from the acid mother liquors from the preparation of salvin chloride, by saturating these with amyl alcohol, when, on standing for a few days, salvianin chloride separated in fine long needles; or directly from salvianin chloride, by allowing its solution in concentrated aqueous hydrochloric acid to stand for several weeks. Any pelargonidin chloride or salvin chloride present in the product was removed by dissolving the crystals in 1 per cent. aqueous hydrochloric acid (0·3 gr. in 50 c.c.) and repeatedly shaking with amyl alcohol. After filtration of the aqueous layer and making the acid in it up to 2 per cent. HCl, on standing for about a day the salvinin chloride separated almost quantitatively. It may be recrystallised from warm 2 per cent. hydrochloric acid, from which it separates in needles, or by dissolving in 0·5 per cent. hydrochloric acid and saturating the solution with amyl alcohol. The crystalline compound is a hydrate of the composition $C_{27}H_{31}O_{15}Cl$, $5H_2O$, whereas pelargonin chloride crystals, when prepared in a similar manner, have the composition $C_{27}H_{31}O_{15}Cl$, $4H_2O$.

Salvinin chloride is fairly soluble in water and in ethyl alcohol, even more so in methyl alcohol, and the solutions are orange in colour at first, but change to violet and, if very dilute, finally become colourless. In cold 1—2 per cent. hydrochloric acid it is difficultly soluble, but easily soluble in warm, and crystallises out from such solutions on cooling in long purple-red needles. In cold 7 per cent. sulphuric acid it is very difficultly soluble, but dissolves easily in the hot acid (7 per cent.), and on cooling clusters of needles separate. No characteristic colour reaction is given with ferric chloride. Picric acid gives a scarlet-red amorphous picrate.

The distribution number of salvinin chloride is as that of normal diglucoside anthocyans, viz. about 1—2. The pure product sinters at 167° C. and melts, with decomposition, at 168° C.

On complete hydrolysis salvinin chloride yields *pelargonidin* (1 molecule) and *glucose* (2 molecules), but in the course of the hydrolysis the production of an intermediate monoglucoside was ob-

served by Willstätter and Bolton, which resembled pelargonenin (see above), but was considered by them to be isomeric, not identical with it. The data available on this point are, however, very scanty, and the new substance has not been completely examined.

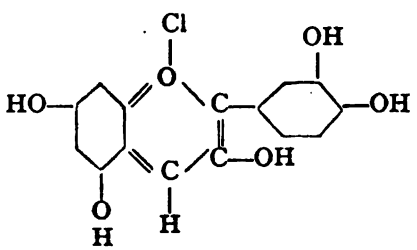
It is of interest to note that of the pelargonidin derivatives so far examined, salvianin, salvin, pelargonin, pelargonenin, and the monoglucoside obtained from salvinin by partial hydrolysis, show fluorescence when in acid alcoholic solution, whereas callistephin does not.

Cyanidin and its Derivatives.

Glucosides of cyanidin occur in a variety of flowers and fruits. It was first isolated by Willstätter and Everest, from the corn-flower (*Centaurea cyanus*), and was the first sugar-free anthocyan to be obtained in a state of purity; it has since been obtained from the petals of *Rosa gallica*, peony, chrysanthemum (*Chrysanthemum indicum*, Linn.), dahlia (deep-red), aster (*Callistephus chinensin*, Nees, syn. *Aster chinensis*, Linn.), poppy (*Papaver rhoeas*, Linn.), and from the fruit of the cherry (*Prunus avium*, Linn.), cranberry (*Vaccinum vitis idaea*), and sloe (*Prunus spinosa*, Linn.), whilst, as the result of qualitative tests, Willstätter and Bolton (Annalen, 1916, 412, 138) consider that cyanidin derivatives are present in the flowers of *Zinnia elegans*, Jacq., Hybrid Gladiolas, *Gaillardia bicolor*, Hook., *Helenium autumnale*, Linn., *Tulipa gesneriana*, Linn., *Tropæolum majus*, Linn., and the berries of the red currant (*Ribes rubrum*, Linn.), raspberry, and mountain ash. In some of these cases they consider that the cyanidin derivative is accompanied by compounds derived from pelargonidin.

Cyanidin.

Cyanidin is most readily isolated in the form of its chloride which has the composition $C_{15}H_{11}O_6Cl$, and the structure—



and which consists when in the crystalline form of the hydrate $C_{15}H_{11}O_6Cl$, H_2O, from which the water of crystallisation is not lost by drying in air, in a vacuum desiccator, or in high vacuum at 50° C., but is completely given up in high vacuum at 105° C. Both the colour base and the pseudo-base of cyanidin have been prepared in crystalline condition. The anhydrous chloride does not melt at 300° C., whereas that dried at 50° C. in high vacuum melts at once if dipped in a bath at 220° C. If put into a bath at 200° C., and the temperature is then raised, it does not melt.

Cyanidin chloride is readily prepared from any of the naturally occurring glucosides by hydrolysis with hydrochloric acid, or from the glucoside (peonin) or its methyl ether (peonidin) by hydrolysis and demethylation with hydriodic acid. Hydrolysis of the glucosides is best carried out by boiling with 20 per cent. hydrochloric acid for three minutes, when the product separates in long red-brown needles which have a metallic lustre, the separation being almost complete on cooling. The salt may be recrystallised by solution in ethyl alcohol, addition of half its volume of 7 per cent. hydrochloric acid (aqueous) and slow evaporation of the alcohol. When powdered it has a brown-red colour and marks paper a deep violet, and is very soluble in methyl or ethyl alcohol, giving fine violet-red solutions. When an alcoholic solution is mixed with double its volume of water and warmed to about 85° C., the colour gradually changes till finally only a pale brown-yellow remains. This, which is due to pseudo-base formation, only takes place very slowly in the cold; addition of acid to the decolorised solution does not reproduce the colour immediately, but on warming it returns quantitatively.

In dilute hydrochloric acid the salt is very difficultly soluble, even hot, and a solution in 20 per cent. HCl contains only 0·001 per cent. of the pigment; it is fairly soluble in 7 per cent. sulphuric acid, and on cooling crystals of the sulphate separate. With perchloric acid a well-crystallised salt is formed which is very soluble in ethyl alcohol and separates on evaporation of the solvent in large deep-red prisms.

This colouring matter, like other anthocyanidins, is quantitatively extracted from an aqueous acid solution by shaking with amyl alcohol. The amyl alcoholic extract when shaken with sodium acetate becomes violet, whilst if shaken with aqueous sodium carbonate the colour changes to blue and passes to the aqueous layer. The fine red solution of the pigment in moist amyl alcohol is not very stable, becoming yellow-brown when left for a few days.

An aqueous, or dilute alcoholic acid solution of the chloride on addition of sodium carbonate becomes violet, then blue—if any pseudo-

base is present it changes to green; addition of potassium acetate to an alcoholic solution produces a violet-blue precipitate; lead acetate gives an amorphous blue precipitate. Ferric chloride with an alcoholic solution of the pigment gives a pure blue, whilst if added to an aqueous solution it produces a violet coloration; excess of the reagent causes rapid oxidation and the colour changes to yellow. When the chloride is boiled with hydriodic acid it passes into solution and on cooling the iodide crystallises out. Zeisel estimations have shown the absence of methoxy groups in the compound.

Willstätter and Everest found that careful oxidation with hydrogen-peroxide converted cyanidin chloride into a yellow crystalline compound that had properties resembling those of a flavonol. When decomposed by means of melted alkali, cyanidin chloride yields *phloroglucinol* and *protocatechuic acid.*

The absorption spectrum was examined by Willstätter and Everest, who described it as consisting of one broad band reaching from the yellow to blue, the edges being ill-defined. The following data were given by them:—

1 mol. in 2500 litres	. layer	2·5 mm.	577—520 . . . 507
		5·0 „	583—486
		10·0 „	589—474

Cyanidin Colour Base.—This was obtained as a flocculent precipitate by Willstätter and Everest, and later in a crystalline condition by Willstätter and Nolan (Annalen, 1915, 408, 13), by mixing a hot concentrated solution of cyanidin chloride in alcohol with twice its volume of water. When finely powdered the violet base thus obtained is fairly soluble in alcohol and more so in pyridine, but its solution in the latter becomes rapidly decolorised.

Cyanidin Pseudo-Base $C_{15}H_{12}O_7$.—This substance can be obtained in the form of its crystalline hydrate $C_{15}H_{12}O_7$, H_2O. 0·5 gr. cyanidin chloride is dissolved in 820 c.c. of alcohol and twice the volume of water added. The liquid becomes violet-red, but practically no precipitate of the colour base is formed, and when heated gently for half an hour the colour changes to pale yellow-red, after which the alcohol is rapidly distilled off, *in vacuo*, on a water-bath, the solution saturated with ammonium sulphate and extracted with ether. The ethereal solution of the base is decolorised with animal charcoal and concentrated, after which some 0·35 gr. of the base separates as colourless lens-shaped crystals. The same form is said to be obtained by precipitation of a solution of the base in glacial acetic acid by means of benzol.

The base is readily soluble in water, more so when warm than when cold, but is not easily crystallised from water, as when a concentrated solution is allowed to stand some of the violet colour base is produced. It is easily soluble in alcohol, acetone, or glacial acetic acid, but insoluble in benzol. Sodium carbonate dissolves it with a yellow coloration, whilst treatment of the base with hot or cold 20 per cent. hydrochloric acid slowly produces crystalline cyanidin chloride.

The water of crystallisation in the crystalline hydrate is very difficult to remove; it is not affected by drying in a vacuum desiccator and only commences to come off in high vacuum at about 80° C., dehydration not being complete below 130° C. At this temperature conversion of the pseudo-base to the violet colour base has commenced and the dry product is deep violet in colour.

Derivatives of Cyanidin.

1. *Methyl ether*, and its glucoside, see Peonidin.
2. *Monosaccharides:* Asterin, Chrysanthemin, and Idaein.
3. *Disaccharides*—
   (*a*) Diglucosides: Cyanin and Mekocyanin.
   (*b*) Rhamno-glucosides: Keracyanin and Prunicyanin.

MONOSACCHARIDES.

ASTERIN.

Asterin is one of the pigments of the purple-red aster (*Callistephus chinensis*, Nees, syn. *Aster chinensis*, Linn.), and has been isolated by Willstätter and Burdick (Annalen, 1916, 412, 149), (cf. callistephin).

The colouring matter after separation from the pelargonidin derivative (callistephin) that accompanies it in the flowers as described on p. 268, was finally purified by recrystallisation from aqueous methyl alcoholic hydrochloric acid—containing but a very small per cent. of HCl—by allowing the alcohol to evaporate slowly.

Asterin chloride, $C_{21}H_{21}O_{11}Cl$, forms fine bronze-brown to red-brown crystals (prisms) having metallic lustre, which contain water of crystallisation and have the composition $C_{21}H_{21}O_{11}Cl$, $1\frac{1}{2}H_2O$. Both the anhydrous and hydrated forms are isomeric with the respective forms of chrysanthemin chloride, but the crystals of the two pigments differ greatly.

The salt is soluble in water yielding a brown-red solution which

assumes a more bluish tinge on dilution, then becomes colourless as the result of pseudo-base being formed. It gives reactions identical with those of chrysanthemin chloride in respect of ferric chloride, sodium carbonate, sodium hydrate, and distribution between amyl alcohol and aqueous acid, viz. with ferric chloride in alcoholic solution, a blue coloration; sodium carbonate added to an acid solution gives a violet colour, whilst sodium hydrate produces a blue; the distribution number for this compound resembles that for other monosaccharide anthocyans. On the other hand, it differs greatly from chrysanthemin chloride in respect of its solubility in acids, as may be seen from the following data given by Willstätter and Burdick:—

	EtOH (containing HCl).	0·5 Per Cent. HCl.	3 Per Cent. HCl.	7 Per Cent. HCl.	7 Per Cent. H_2SO_4.
Asterin chloride	Easily soluble cold.	Very easily soluble.	Easily soluble.	Appreciably soluble cold; on slight warming very easily soluble.	Fairly easily soluble.
Chrysanthemin chloride	Fairly difficultly soluble.	Much less soluble.	Difficultly soluble.	Very insoluble, only appreciably soluble boiling, and rapidly separates on slight cooling.	Very easily soluble, much more so than asterin chloride.

On hydrolysis asterin chloride yields cyanidin chloride (1 mol.) and glucose (1 mol.).

CHRYSANTHEMIN.

Chrysanthemin, the pigment of the deep-red chrysanthemum (*Chrysanthemun indicum*, Linn.), has been isolated and described by Willstätter and Bolton (Annalen, 1916, 412, 136), who used deep-red flowers for their investigations (Ruby King), but also found that many scarlet and red garden kinds contained this pigment mixed with various carotinoids.

The pigment closely resembles Idaein (the cranberry pigment) in many of its properties, but the differences in solubility are stated to be sufficient to characterise it.

For the isolation of the colouring matter the petals (those used contained about 7 per cent. of their dry weight of chrysanthemin,

other red sorts examined contained amounts varying from one-half to one-third only of this) were extracted with glacial acetic acid (fifteen times the weight of the petals) for three days and the residue on the filter washed with fresh glacial acetic acid (equal to weight of petals); under these conditions the extraction is said to be almost quantitative. On addition of ether (twice the volume) to the filtered extract a heavy red flocculent precipitate of the colouring matter—as acetate—is produced. (In this case, as in some few others, it is said, to be advantageous to precipitate the pigment as acetate rather then as chloride.)

The purification of the crude chrysanthemin thus prepared was carried out in either of two ways, one making use of the picrate and the other of the distribution between amyl alcohol and aqueous acid. The latter method is more or less generally applicable to monoglucosides of the series on account of their passing to a reasonable extent into the alcoholic layer, but chrysanthemin having a high distribution number for a monoglucoside may even be more advantageously purified by this method than other pigments of the group. On the other hand, even in this case, the very large bulk of solvents required to work up even small quantities of pigment make the method, though of great interest, useless for the purification of the colouring matter in quantity.

For the picrate process the crude acetate (from 2½ kg. of petals) was dissolved in 0·5 per cent. hydrochloric acid (400 c.c.) and twice extracted with amyl alcohol (200 c.c. each time) to remove any free cyanidin that may be present, and the residual traces of amyl alcohol were removed from the aqueous layer by shaking with ether. After this preliminary treatment the aqueous solution of the pigment was mixed with cold saturated picric acid solution (500 c.c.) and allowed to stand for a day when the crude picrate had separated as spherical aggregates (18 gr.). It was then dissolved in methyl alcohol (225 c.c.), filtered, and the solution mixed with 10 per cent. methyl alcoholic hydrochloric acid (40 c.c.), after which ether (ten times the volume) was added to reprecipitate the colouring matter which separates as a brown-red powder (9·7 gr. of 64 per cent. purity). After thrice purifying this product by slow precipitation from alcoholic solution by addition of aqueous hydrochloric acid (7 per cent.), the pigment was finally obtained as chloride in the form of fine microcrystals (prisms and long tablets, 4·5 gr.).

The purification by means of amyl alcohol consists in dissolving the crude product in 0·5 per cent. hydrochloric acid, extracting twice with half the volume of amyl alcohol, to remove any cyanidin, and

rejecting these alcoholic extracts, then extracting further twenty times (each with one volume of amyl alcohol), partially drying the alcoholic extract and precipitating the pigment from it by means of light petroleum, mixing the syrup so obtained with methyl alcohol and completing the precipitation by means of ether. The further purification of the chloride thus obtained was similar to that obtained by the picrate process.

Chrysanthemin chloride, $C_{21}H_{21}O_{11}Cl$, forms a crystalline hydrate having the composition $C_{21}H_{21}O_{11}Cl$, $1\frac{1}{2}H_2O$, which loses its water if dried in high vacuum at 100° C.; the crystals are red-violet pointed rhombic leaflets which have a fine metallic sheen. In a melting-point tube they begin to decompose at 205° C. and blacken, but show no melting-point.

Its acid aqueous, or alcoholic, solutions have the same colour as corresponding solutions of cyanin, idaein, or asterin, but their intensity is about twice that of cyanin solutions.

In water the salt is easily soluble, in methyl alcohol very easily, but in ethyl alcohol rather difficultly soluble, and but little more so when this is hot. In dilute hydrochloric acid it is much less soluble than idaein chloride, as the following figures given by Willstätter and Bolton show: at 17° C. 100 c.c. ½ per cent. HCl dissolves 0·0845 gr. chrysanthemin chloride, but dissolves 8·48 gr. idaein chloride; at 17° C. 100 c.c. 2 per cent. HCl dissolves 0·0604 gr. chrysanthemin chloride, but dissolves 0·7 gr. idaein chloride, whereas in hot ½ per cent. hydrochloric acid chrysanthemin chloride is very easily soluble. It is interesting to note that this salt readily forms super-saturated solutions, and if a concentrated aqueous solution is mixed with an equal volume of 4 per cent. hydrochloric acid, it may stand for weeks before any precipitate of pigment is formed.

In 7 per cent. sulphuric acid it is very easily soluble, much more readily than idaein chloride or cyanin chloride.

The following reactions have been recorded. On addition of sodium carbonate to an acid solution of the chloride a violet colour is produced, whereas caustic soda produces a pure blue; ferric chloride on addition to an alcoholic solution gives a blue colour which on dilution with water passes to violet; calcium chloride causes the precipitation of a blue calcium salt, whilst the lead salt if precipitated from alcoholic solution of the pigment is blue, and if from aqueous solution violet.

The distribution number of this salt is 19, and is therefore high as compared with the majority of monosaccharide anthocyans.

On hydrolysis chrysanthemin chloride yields *cyanidin chloride* (1 molecule) and *glucose* (1 molecule).

Chrysanthemin picrate was prepared by adding 10 c.c. of a saturated solution of picric acid to 20 c.c. of a solution of chrysanthemin chloride (0·3 gr.) and separated freely as thin red prisms which sinter at 155° C., and melt with decomposition at 165° C. The salt is very easily soluble in alcohol, but rather difficultly so in water; its dilute solutions are said to become decolorised even more readily than those of the chloride.

IDAEIN.

Idaein, the colouring matter of the cranberry (*Vaccinium vitis idaea*, Linn.), the berries of which contain about 0·035 per cent. of their weight of the pigment, has been subjected to examination by Willstätter and Mallison (Annalen, 1915, 408, 15), who succeeded in isolating it in a finely crystalline condition.

For the preparation of the pure colouring matter the skins of the berries only were made use of, as the major portion of the pigment occurs in them. 138 kg. of berries gave 34 kg. of skins (containing about 76 per cent. of water), and these were worked up in lots of about 11 kg. at a time, such a quantity being left with 17 litres of glacial acetic acid in a closed vessel for eight days in order to extract the pigment, and, after filtration, a further 8 litres was used to wash the residue. The filtrate (25 litres) was divided into portions and the pigment precipitated by the addition of ether (two and a half times the volume) and shaking for twenty minutes, after which the upper layer was decanted from the deep red syrup. This was dissolved in warm glacial acetic acid (2 litres) and the solution diluted with a further quantity of the acid (2 litres); after filtration, the solution thus obtained was fractionally precipitated by means of ether, the first oily precipitate being neglected, and the second fraction, which contains the bulk of the colouring matter, collected, washed with ether, and converted into picrate by dissolving in water (300 c.c.) and mixing the solution with a solution of picric acid (20 gr.) in warm water. The first flocculent precipitate that appeared whilst still hot was rapidly filtered off, and the solution on cooling then deposited a mixture of crystals of the colour picrate and potassium picrate. For preparation of the pure chloride the picrate was not further purified, but if the pure picrate was desired, the above product was dried, dissolved in warm methyl alcohol, in which potassium picrate is not readily soluble, and the solution precipitated by ether. It was then further purified by recrystallisation from water. For pre-

paration of the chloride the impure picrate was dissolved in boiling methyl alcohol (150 c.c.) and such an excess of methyl alcoholic hydrochloric acid (30 c.c., 17 per cent. HCl) added that about 2 per cent. free hydrochloric acid remained in the solution, and the chloride then precipitated by addition of ether (1 litre), the precipitate being washed free from picric acid by means of ether. 10·7 kg. of skins yielded 1·6 gr. of idaein chloride, i.e. about 17 per cent. of the total pigment present in the original acetic acid extract. The product was recrystallised by dissolving in water (0·5 gr. in 50 c.c.), adding concentrated hydrochloric acid (10 c.c.), filtering off the small amount of flocculent precipitate, then adding ethyl alcohol (20 c.c.) and allowing the alcohol to evaporate off slowly, when the chloride separates in fine leaflets with a metallic lustre. A further recrystallisation was found to be advantageous.

Idaein chloride, $C_{21}H_{21}O_{11}Cl$, forms a crystalline hydrate having the composition $C_{21}H_{21}O_{11}Cl$, $2\frac{1}{2}H_2O$, which is described as forming brown-red monoclinic prisms with a green metallic lustre. It loses all its water of crystallisation when dried in a vacuum desiccator at ordinary temperature, melts with frothing at 210° C., and differs considerably from cyanin in its solubility.

In water it is very easily soluble—1 in 10 at 15° C.—yielding a deep brown-red solution which on dilution passes to orange-red—very dilute solutions show decolorisation, but do not appear to become completely decolorised, a pale rose colour remaining. In alcohol the salt is readily soluble producing a bluish-red solution; in hydrochloric acid of very low concentration (e.g. $\frac{1}{2}$ per cent.) it is easily soluble, but in 6 per cent. it is almost insoluble; in sulphuric acid it is more soluble than in hydrochloric acid, 7 per cent. acid dissolves 0·03 gr. in 100 c.c. at 25° C., but warm solutions on cooling deposit crystals of the sulphate.

The following reactions have been recorded by Willstätter and Mallison. With sodium carbonate an acid solution of the salt passes to violet which is stable in excess of the reagent, whilst with caustic soda a blue colour is produced that rapidly passes to green, then to yellow; ferric chloride added to an alcoholic solution gives a blue coloration which on dilution passes to violet; alum produces a very stable violet colour when added to an aqueous solution, whilst bismuth nitrate gives a red-violet coloration. Zinc (or copper) acetate on addition to an alcoholic solution produces a blue coloration, whilst to an aqueous solution the addition of copper (or lead) acetate gives a red-violet precipitate; lead acetate added to a solution in alcohol gives a blue precipitate. Zinc and hydrochloric

acid (or sodium hydrosulphite) decolorise a solution of the pigment, and treatment of the resulting solution with air, or hydrogen peroxide, causes the return of the colour.

Idaein chloride has a distribution number about 10, i.e. behaves as a normal monosaccharide anthocyan, and on hydrolysis it yields *cyanidin chloride* (1 molecule) and *galactose* (1 molecule). It will be noticed that in respect of the distribution number of saccharide pigments of this series containing it, galactose appears to resemble glucose in its effect, and differs from rhamnose.

Willstätter and Mallison describe the absorption spectrum as consisting of one broad band resembling that of cyanin, but reaching less far into the blue. They obtained the annexed results. Solution containing 1 molecule in 2500 litres of 7 per cent. sulphuric acid,

Thickness of layer 2·5 mm.	.	.	556 . . . 542—476
„ „ „ 1·25 „	.	.	546 . . 530— —484

Idaein chloride is optically active, and the following measurements are on record:—

Dilute solution in 0·5 per cent. HCl, monochromatic light

$$[\alpha]_e = -219^\circ (\pm 15^\circ);$$

more concentrated solution, white light (1000 c.p. Osram globe 23 cms. away)

$$l = 0{\cdot}5\ [\alpha] = -378^\circ (\pm 5^\circ);\ l = 1{\cdot}0\ [\alpha] = -342^\circ (\pm 5^\circ).$$

Idaein picrate forms microscopic red needles. It is soluble in 30 parts of boiling water, very insoluble in cold water, the solutions being orange-red; it is soluble in ethyl alcohol yielding cherry-red solutions—very dilute solutions in either solvent show loss of colour with formation of pseudo-base, unless excess of picric acid is present. If a drop of the aqueous solution be placed on filter paper it produces a spot with violet centre and yellow exterior, as the result of hydrolytic dissociation.

Idaein sulphate is described as forming bright brown rhombic crystals when a solution of the chloride in warm sulphuric acid (7 per cent.) is allowed to cool.

Disaccharides. (*a*) Diglucosides.

Cyanin.

Cyanin, the colouring matter of the corn-flower (blue and deep purple), *Rosa gallica*, deep red dahlia, etc., has been the subject of several investigations, of which the earliest was carried out by F. S. Morot in 1849 (Ann. d. sciences nat., (3), 13, 160 (1849-50)). The work of Morot is of interest in that he attempted to prepare the

pigment by precipitation from aqueous solution by means of alcohol, a process which formed a portion of the method of purification whereby Willstätter and Everest obtained the pure pigment. In addition to the work of Morot, that of Fremy and Cloëz (J. pr. Chem., 1854, 62, 269) should be mentioned, as they included the pigment of the corn-flower in their investigation of the colouring matters of flowers. They gave to it, in common with the other pigments examined, the name cyanin, and this was adopted by Willstätter and Everest for the corn-flower pigment when, in 1913 (Annalen, 401, 189), they succeeded in preparing it in a pure and crystalline condition, a result that paved the way for the great advance in our knowledge of the anthocyan pigments that has since been achieved. Although this colouring matter was first obtained from the petals of the blue corn-flower, *Centaurea cyanus*, it is much more readily prepared from *Rosa gallica* or deep red dahlia petals.

The isolation of cyanin from blue corn-flowers is a long and tedious process, consisting of repeated, rapid fractional precipitation of an aqueous extract of the petals by means of alcohol, followed by conversion of the partially purified blue pigment into the chloride (red) and slow fractional precipitation of its solution in alcoholic hydrochloric acid by means of ether. The amorphous, but almost pure product is then crystallised by solution in alcohol, addition of aqueous hydrochloric acid, and slow evaporation of the alcohol. Although it was not found possible to obtain the blue pigment itself in a pure condition, fractional precipitation yielded it so sufficiently to prove that before conversion into the chloride, it was present as a potassium salt, and that in this form it occurs in the blue corn-flower.

Much simpler methods are available for its isolation from other flowers—rose, dahlia, or deep bordeaux coloured corn-flower; but all efforts to improve the method used by Willstätter and Everest for its preparation from the blue corn-flower have hitherto failed. The flowers mentioned contain: corn-flower (blue), about 0·75 per cent., (deep violet-blue), 3·6 per cent., (deep bordeaux), 13—14 per cent.; dahlia (deep red), about 20 per cent.; rosa gallica, 2 per cent., respectively, of their dry weight of cyanin. Willstätter and Mallison consider the petals of the deep red dahlia to be the best source of the pigment.

In 1878 Senier (J. Pharm., (3), 7, 650 (1878)), made an attempt to isolate the pigment of the rose, using the lead salt method, but failed, and ascribed his failure to the fact that the precipitation of

the lead salt was not sufficiently specific. In 1905 Molisch (Bot. Ztg., 157) succeeded in preparing this colouring matter in micro-crystalline form in the same way that he had obtained crystals of the pelargonium pigment, but it remained for Willstätter and Nolan (Annalen, 1915, 408, 1) to obtain it pure and crystalline in quantity, and to establish its identity with the cyanin previously isolated by Willstätter and Everest from the corn-flower. From 1 kg. of dry petals (commercial, rosa gallica) they were able to obtain 7 gr. of pure crystalline cyanin chloride. Their process consisted in extracting the petals with methyl alcoholic hydrochloric acid (about 2 per cent. HCl) — ethyl alcohol is not so satisfactory (1 kg. to 3 litres)—filtering after some sixteen hours, washing the residue with further solvent (1 per cent. HCl, 500 c.c.) several times to complete the extraction, and precipitating the filtrate (5 litres) by mixing it with two and a half times its volume of ether, when the pigment separates as a gummy mass. The best method of obtaining the pure pigment from this crude product (amount from 1 kg. of petals taken at a time) consists in allowing it, without drying, to stand for twenty-four hours with alcoholic hydrochloric acid, or better, with methyl alcohol (200 c.c.) and glacial acetic acid (140 c.c.), when the impurities present become hydrolysed or acetylated, but the cyanin remains unchanged as a deep brown micro-crystalline residue. The product is dissolved in boiling water (700 c.c.), mixed with an equal volume of 3 per cent. ethyl alcoholic hydrochloric acid and allowed to cool, when cyanin chloride separates in fine glistening crystals (about 6·5 gr.), and a further crop may be obtained from the mother liquors.

From the deep red dahlia flowers cyanin chloride is readily prepared in quantity as described by Willstätter and Mallison (Annalen, 1915, 408, 147), (*note*—scarlet-red dahlia flowers yield pelargonin), in that an extract of the fresh flowers (700 gr.) in glacial acetic acid is first mixed with methyl alcoholic hydrochloric acid, then precipitated with ether (one and a half volumes), which produces a flocculent deposit that congeals together, and when dried (15 gr.) is 76 per cent. pure. This on solution in cold 7 per cent. hydrochloric acid (300 c.c.), filtration and standing, yields the chloride in a crystalline condition, which may be recrystallised in the same way described as the product obtained from rose petals. The yield from 700 gr. fresh petals is about 7·4 gr. pure crystalline chloride (air-dried), i.e. 50 per cent. of the total amount present in the petals.

To obtain cyanin chloride from deep bordeaux coloured corn-flowers Willstätter and Mallison extracted these with glacial acetic acid, and added ether, when an oily product was deposited, which when dissolved in a little 7 per cent. hydrochloric acid after a day, separated in a granular condition. The product washed with hydrochloric acid was recrystallised from warm 3 per cent. aqueous hydrochloric acid when it separated in glistening rhombic-shaped tablets, which appear violet under the microscope, and have a melting-point 198° C.

Cyanin chloride, $C_{27}H_{31}O_{16}Cl$, crystallises in the form of red-brown rhombic leaflets which contain $2\frac{1}{2}$ molecules of water of crystallisation ($C_{27}H_{31}O_{16}Cl \cdot 2\frac{1}{2}H_2O$), of which some $\frac{1}{2}H_2O$ remains in the product when dried in high vacuum at 50° C., but all is lost when dried in this way at 105° C.

The air-dried crystalline chloride is almost insoluble in cold water, but dissolves very readily at 90° C. By the addition of an equal volume of 3 per cent. ethyl alcoholic hydrochloric acid to the solution, the salt is almost completely precipitated, separating as aggregates of leaflets with a golden reflex. The salt is only slowly and difficultly soluble in cold ethyl alcohol (100 c.c. at 19° C. dissolve 0·053 gr. of crystals from the rose, 0·059 gr. crystals from the corn-flower), very difficultly soluble in acetone and chloroform and insoluble in benzene. In dilute hydrochloric acid it is but little soluble, as the following figures indicate :—

100 c.c. 1 p.c. HCl at 20° C.			diss.	0·015	gr.	air-dried	crysts.	from	rose.
			,,	0·015	,,	,,	,,	,,	corn-flower.
,,	1½ p.c. HCl	,,	,,	0·0053	,,	,,	,,	,,	rose.
			,,	0·0055	,,	,,	,,	,,	corn-flower.

and these figures have been used by Willstätter and Nolan (Annalen, 1915, 408, 1) as evidence of the identity of the pigment from the corn-flower and rose. In 7 per cent. sulphuric acid the crystalline chloride is fairly readily soluble, but on standing, the sulphate always crystallises out; thus a solution of 0·01 gr. of chloride in 30 c.c. deposits this in thin deep red needles.

Dilute aqueous, or alcoholic, solutions of the salt become decolorised as the result of pseudo-base formation, but addition of acid to the decolorised solution causes quantitative return of the colour. The decolorised solution gives a yellow colour on addition of sodium carbonate and a green precipitate with lead acetate; excess of sodium carbonate or caustic soda changes it to a yellow which does not become red on addition of acid.

The following reactions of cyanin chloride have been noted:—

Ferric chloride when added to an aqueous solution produces a fine violet coloration, whereas in alcoholic solution a beautiful intense blue results; with excess of the reagent the colour rapidly fades, passing finally to yellow; lead acetate completely precipitates the colour from its solutions producing violet-blue flakes which have a copper-coloured reflex. When the lead salt thus prepared is treated in the presence of water with carbon dioxide, or with a limited quantity of sulphuretted hydrogen, a blue solution results, and appears to contain a primary lead salt which can be obtained from the solution by precipitation with alcohol. With alkalis (sodium carbonate or caustic soda) an acid solution of cyanin chloride passes through violet to a fine pure blue, whereas with calcium carbonate the reaction passes only to the violet stage, the violet solutions thus formed becoming rapidly decolorised owing to pseudo-base formation. Zinc and dilute acetic acid (or HCl, or H_2SO_4) reduce the salt with formation of a colourless leuco compound from which the colour may be regenerated by air oxidation; sodium bisulphite produces a colourless soluble compound which is decomposed by addition of acid with liberation of the pigment; Fehling's solution, even hot, is not reduced by cyanin chloride.

The absorption spectrum was described by Willstätter and Everest as consisting of one broad band covering a large portion of the green and blue. A solution of 1 mol. in 2500 litres gave the following figures:—

Thickness of layer 2·5 mm. . .	549·540—467·462
„ „ „ 5·0 „ . .	561·553—448

Cyanin chloride is optically active, and Willstätter and Nolan obtained the subjoined values when using white light (1000 c.p. ½ watt Osram lamp):—

Pigment from corn-flower	$[\alpha] = -225°$ and $-251°$
„ „ rosa gallica	$[\alpha] = -249°$ and $-267°$

They consider the most probable value to be $[\alpha] = -258° (\pm 10°)$.

The distribution number of cyanin chloride (1·8) is normal for a diglucoside anthocyan, and on hydrolysis the salt yields *cyanidin chloride* (1 mol.) and *glucose* (2 mols.).

Cyanin picrate is very readily soluble in water and is difficult to prepare, but may be obtained by suspending cyanin chloride in a little water and adding a saturated solution of picric acid in the same solvent. The pigment goes into solution, and on standing

for several days a flocculent precipitate separates which consists of fine red needles.

In dilute aqueous solution the picrate readily undergoes isomerisation, the change being complete on warming; in alcohol it is readily soluble without undergoing change.

Cyanin potassium salt.—This compound, which is the actual blue colouring matter of the wild corn-flower, was obtained by Willstätter and Everest in a state of considerable purity, and finally in a crystalline condition by slow evaporation of a concentrated solution in 20 per cent. aqueous sodium chloride, after this had been purified by dialysis. The cyanin salt separated in fine deep blue six-sided tablets, but could not be completely freed from sodium chloride as small quantities only were available. On the other hand, it was necessary to use solutions in strong sodium chloride (or nitrate) solution for the dialysis, as otherwise the whole of the cyanin salt became isomerised before purification was complete.

The salt is very soluble in water, giving beautiful blue solutions, which, however, become decolorised on standing. The decolorisation is greatly retarded by the addition of various inorganic salts, and solutions containing 20 per cent. of common salt can be kept for months without decolorisation occurring. Addition of acid to the blue solution, or to the colourless one produced from it by standing, gives a red coloration. The addition of sodium carbonate to a blue solution causes no immediate change of colour, but if the liquid has stood before the sodium carbonate is added, a blue-green to green-blue colour results, whereas addition of the carbonate to a solution that has become colourless by standing produces a yellow colour. The salt is insoluble in alcohol, ether, and benzene, but fairly readily soluble in ethylene glycol. The colour is stable to light.

Mekocyanin.

Mekocyanin is one of the pigments of the poppy (*Papaver rhoeas*, Linn.)—a double purple-scarlet garden variety.

This has been isolated and described by Willstätter and Weil (Annalen, 1916, 412, 231), who state that it occurs in the flowers together with a second pigment which they have not, as yet, completely investigated. The petals used contained a total of about 18 per cent. of their dry weight of pigment.

The colouring matter was isolated in the form of its chloride, for which purpose the whole petals—including the darker central portions—were used, as preliminary experiments showed that extracts of the

darker portions at the centre of the petals had the same properties as those of the outer parts. The separation of mekocyanin from the other anthocyan that accompanies it was readily accomplished by taking advantage of the unusual great solubility of the former.

For the isolation of the pigment it is said to be necessary to use fresh petals, as there is great difficulty in purifying the colouring matter after extraction from the dried material. The process used by Willstätter and Weil may be described thus: From some 7—8 kg. of fresh poppy petals about 20 litres of extract were obtained on treatment with glacial acetic acid, and to this some 200 c.c. of 10 per cent. methyl alcoholic hydrochloric acid was added before precipitation of the pigment by means of ether, for which purpose 40 litres were required. After standing for a time the clear liquid was decanted, the residue collected, dissolved in water (650 c.c.) and the solution mixed with absolute alcohol (2 litres), to precipitate the impurities present which are difficultly soluble in alcohol. After removal of the latter, a further quantity of 10 per cent. ethyl alcoholic hydrochloric acid (500 c.c.) was added and the colouring matter then precipitated by addition of ether (3 times total volume of liquid), the product obtained in this way being a syrup from which the mother liquors could be readily decanted. In order to separate the mekocyanin from the other component (less soluble in alcohol), the syrup was twice washed with absolute alcohol (1 litre each time) containing 3 per cent. of hydrochloric acid, whereby some 38 gr. of residue was left which contained but little mekocyanin. It was then precipitated from the alcoholic liquors by means of ether (3 times the volume of the solution), collected and dried.

The next purification consisted in allowing the product to stand with 3 per cent. alcoholic hydrochloric acid, when it first passed into solution, and was then reprecipitated as a spongy mass. In about two days the whole was thus transformed and was then collected (26 gr. dry). On dissolving this product, without drying, in 0·3 per cent. hydrochloric acid (90 c.c.) and gradually adding glacial acetic acid (1300 c.c.) the pigment began to separate as flakes, then in spherical forms (13 gr.), and further precipitation was caused by addition of more glacial acetic acid, this fraction consisting of regular spherical garnet-like grains ("kuglig kantigen granatähnlichen Körnern"). Ether now caused the separation of a further quantity of impure product.

The middle fraction described above, although not distinctly crystalline, was used for characterisation and for analyses, whilst the first and last fractions were used for the preparation of the non-glucosidal

compound (cyanidin). Further purification by formation of the crystalline ferrocyanide, reconversion of this into the chloride, and careful precipitation of the latter from aqueous HCl solution, by acetone, yielded the pigment (as chloride), in the form of sharply cut, well-formed needles.

Mekocyanin chloride, $C_{27}H_{31}O_{16}Cl$, forms a hydrate containing 3 molecules of water—$C_{27}H_{31}O_{16}Cl$, $3H_2O$, from which two are readily removed, the third only on drying in high vacuum at 105° C. The salt is very easily soluble in water, dilute solutions becoming decolorised owing to the formation of pseudo-base, and differs greatly from cyanin chloride and the chlorides of other cyanidin saccharides, except prunicyanin chloride, in that it is very easily soluble in aqueous hydrochloric acid (0·01 per cent. to 10 per cent. or even higher). In ethyl alcohol it is difficultly soluble, but rather more soluble in methyl alcohol, and if the chloride is rubbed with either of these solvents containing a small per cent. HCl, it dissolves and is reprecipitated as a voluminous spongy mass. In acetone the salt is insoluble, but is easily soluble in a mixture of acetone and water—this is equally true of most anthocyanin chlorides, and such a mixture is often to be preferred to a mixture of alcohol and water for the recrystallisation of these oxonium salts. In colour the solutions in aqueous acid or in alcohol of mekocyanin chloride are the same as those of cyanin chloride, but the reactions of the pigment are different. Thus, with sodium carbonate it gives a violet colour with slight bluish tinge — cyanin gives blue, keracyanin red-violet — but with caustic soda a corn-flower-blue is produced. With ferric chloride mekocyanin chloride gives the same colour reactions as cyanin chloride.

With regard to distribution between aqueous acid and amyl alcohol, mekocyanin behaves as a normal diglucoside anthocyan, and on complete hydrolysis it yields *cyanidin chloride* (1 mol.) and *glucose* (2 mols.), but, by carefully regulating the conditions of hydrolysis, Willstätter and Weil were able to stop the reaction at an intermediate stage at which a monoglucoside (1 mol.) and glucose (1 mol.) had been produced. The monoglucoside thus isolated was identified by them as *chrysanthemin chloride*, and from this, by hydrolysis, they obtained cyanidin chloride (1 mol.) and glucose (1 mol.).

Mekocyanin ferrocyanide.—This is a highly crystalline characteristic salt, which is readily prepared from the chloride by treating 2 gr. dissolved in 20 c.c. hot 0·3 per cent. hydrochloric acid, with 2 gr. of finely powdered potassium ferrocyanide (added all at once) and allowing the mixture to stand overnight. The amorphous precipitate that first separates has by that time passed to a mass of fine red-brown

needle-shaped crystals (0·9 gr.). The salt is fairly soluble in water, sparingly soluble in alcohol. It can be reconverted into the chloride by treatment with picric acid, filtering off the ferrocyanic acid which separates, and adding ethyl alcoholic hydrochloric acid and ether to the filtrate.

Disaccharides. (*b*) Rhamnoglucosides.

Keracyanin.

Keracyanin, the colouring matter of the sweet cherry (*Prunus avium*, Linn.), has been isolated and described by Willstätter and Zollinger (Annalen, 1916, 412, 164).

For the isolation of the colouring matter the fruit was stoned, the skins rapidly separated from the flesh, and extracted by standing in closed vessels with glacial acetic acid. The skins of 150 kg. of cherries thus yielded 15 litres of extract from which the pigment was precipitated in the form of a syrup by means of ether.

The method given for the purification of the pigment is complicated, and stated to be merely of a temporary character, but it sufficed for the isolation of the pigment in pure and crystalline condition, and permitted at least of a preliminary examination of the compound. This involved fractional precipitation of the crude pigment dissolved in methyl alcoholic hydrochloric acid, by means of ether, followed by its conversion into lead salt; the decomposition of this with recovery of the pigment, and finally further fractional precipitation of a solution of the latter in methyl alcoholic hydrochloric acid by means of ether. The colouring matter was finally obtained in deep bronze-brown clusters of crystals.

Keracyanin chloride, $C_{27}H_{31}O_{15}Cl$, forms crystalline hydrates, of which Willstätter and Zollinger describe two, viz.: $C_{27}H_{31}O_{15}Cl, 4H_2O$ (which loses $3H_2O$ when dried in vacuum desiccator) and

$$C_{27}H_{31}O_{15}Cl, 3H_2O$$

(which loses $1\frac{1}{2}H_2O$ in vacuum desiccator), both of which become anhydrous if dried in high vacuum at 105° C. The former hydrate was obtained when 1·3 gr. of the pure chloride were dissolved in 10 c.c. of very dilute hydrochloric acid, and the solution mixed with 20 c.c. of 10 per cent. HCl; on standing for several days, the compound was precipitated in the form of bright red flakes composed of very fine needles. The second hydrate was prepared by taking 0·85 gr. of the pure chloride dissolved in 8 c.c. methyl alcohol, and adding

16 c.c. of 7 per cent. aqueous hydrochloric acid. It crystallised from this solution in short brown-yellow prisms.

Acid aqueous, or alcoholic, solutions of keracyanin chloride closely resemble those of cyanin chloride in colour, but differ in their reaction with sodium carbonate, with which keracyanin gives a red-violet colour. With caustic soda it gives a blue colour like cyanin; whereas ferric chloride, when added to an alcoholic solution of the salt, gives a blue coloration, which on dilution with water becomes blue-violet (stable).

The salt is easily soluble in hot water, decolorisation taking place —due to pseudo-base formation—in dilute solutions, as with other pigments of the series; in methyl alcohol, even when cold, it is very easily soluble, and in ethyl alcohol fairly easily. It is less soluble in acids than mekocyanin chloride and more so than cyanin chloride, and it is interesting to note that whilst it is difficultly soluble in cold hydrochloric acid of concentrations between 0·01 per cent. and 0·1 per cent., it is easily soluble in 1 per cent. HCl. As the concentration increases beyond this the solubility decreases, until 3 per cent. dissolves but little, and in cold 7 per cent. HCl it is very difficultly soluble, though considerably so if the acid is hot.

On hydrolysis keracyanin yields *cyanidin chloride*, *glucose*, and *rhamnose*, approximately in molecular proportions, but, as previous investigators have found in the case of other rhamno-glucosides—e.g. rutin—Willstätter and Zollinger observed, in the analytical data obtained, some variation from the theoretical proportions of the sugars required for a simple rhamno-glucoside of cyanidin, though evidence points to its being such a compound.

It is of interest to note that in common with the other rhamno-glucoside anthocyans—violanin and prunicyanin—keracyanin has a distribution number (viz. 6·7) approximating to that of a normal *mono*glucoside.

PRUNICYANIN.

Prunicyanin, the pigment of the sloe (blackthorn, *Prunus spinosa*, Linn.), is a compound that closely resembles mekocyanin.

A certain amount of information has been obtained concerning this pigment by Willstätter and Zollinger (Annalen, 1916, 412, 164), but the results published are only preliminary, and the colouring matter has not, as yet, been obtained in a crystalline condition. Only the skins of the fruit were used for the preparation of the pigment, these being extracted with glacial acetic acid, and after addition of alcohol, the colouring matter precipitated by means of

ether. After several fractional precipitations from alcoholic solution by addition of ether, various methods of purification were resorted to, and the pigment finally obtained as small spherical particles—"kuglig kryst. Gebilde".

Prunicyanin chloride, thus prepared, closely resembles mekocyanin in most of its properties, viz. an acid solution on addition of sodium carbonate gives a bluish-violet colour, with caustic soda blue; ferric chloride added to an alcoholic solution produces a pure blue coloration. Like mekocyanin chloride, it is unusually soluble in hydrochloric acid of various concentrations, and also has the interesting property of passing into solution in a small quantity of cold ethyl alcohol and being again deposited from this in a bulky sponge-like form—possibly micro-crystalline. It differs from mekocyanin chloride in having a distribution number (viz. 9·5) very close to that obtained for normal *mono*glucoside anthocyans, but as hydrolysis of prunicyanin chloride, together with pentose estimations, prove that it yields *cyanidin chloride*, *rhamnose*, and a *hexose* (not yet identified), probably in molecular proportions, the high distribution number is not explained by its being a monosaccharide, but by the presence of rhamnose in the molecule (cf. keracyanin and violanin).

Cyanidin Monomethyl Ether.

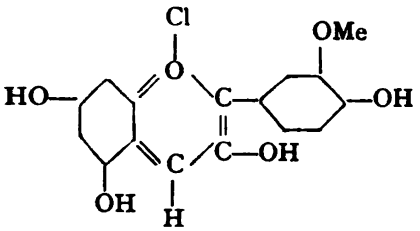
Peonidin.

This substance occurs in the form of its diglucoside (peonin) in the flowers of the deep violet-red peony, and has been obtained from it by Willstätter and Nolan, who found that the hydrolysis of the glucoside is best carried out by rapidly heating 0·5 gr. peonin chloride in a boiling solution with 75 c.c. of 20 per cent. hydrochloric acid, and when complete solution occurs, boiling for exactly five minutes, by which time the peonidin has almost completely separated as crystalline chloride, and is collected while hot, and washed with 20 per cent. hydrochloric acid. It was found that shorter hydrolysis tends to leave unchanged glucoside, whilst too prolonged action of the acid partially attacks the methoxy group.

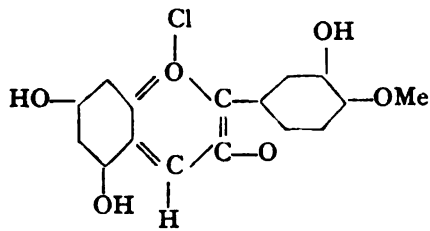
Peonidin chloride, $C_{16}H_{13}O_6Cl$, forms a crystalline hydrate of the composition $C_{16}H_{13}O_6Cl$, H_2O, which consists of long red-brown needles similar in form to the crystals of cyanidin chloride, but differing from them in that the water of crystallisation in peonidin chloride is

completely removed by drying in vacuum desiccator at room temperature.

The anhydrous chloride is considered by Willstätter and Nolan to have the structure (1) or (2) in that alkaline decomposition



(1)



(2)

has shown that the methoxy group is attached to the hydroxyphenyl group. Further, as sodium carbonate gives a blue colour when added to an acid solution of the pigment—this they regard as evidence of a free OH in the pyrylium ring—and ferric chloride gives no colour reaction, they consider that the attachment of the methyl to one of the OH groups of the catechol residue is certain. Of the two formulæ, they regard (1) as more probably correct.

Peonidin chloride is fairly soluble in cold water, very soluble in hot; on boiling the solutions become decolorised, but addition of dilute acid causes the colour to return, slowly if cold, rapidly and quantitatively if hot. In alcohol it is very soluble, forming a fine violet-red coloured solution which differs from that of cyanidin chloride in that the addition of water causes the colour to change to brownish-red, without formation of any precipitate, whereas similar treatment of a cyanidin chloride solution causes the separation of a flocculent violet precipitate. In 1 per cent. hydrochloric acid the salt is very difficultly soluble cold, but easily soluble hot, and may readily be recrystallised from this medium; its solubility in 7 per cent. sulphuric acid is very similar, but in this case crystals of the sulphate separate from warm solutions on cooling.

Sodium carbonate, when added to an acid solution of peonidin chloride, produces a blue colour, whereas potassium acetate causes the colour of an alcoholic solution to become violet, and on diluting with water a red-brown precipitate forms, the liquid remaining violet-red (cyanidin chloride solutions similarly treated yield a finely divided violet precipitate). Ferric chloride produces no characteristic colour on addition to an alcoholic solution, only a slight change to violet-red being observable.

Zeisel estimations proved that peonidin chloride contains one methoxy group in the molecule, and when the finely crystalline iodide of the methoxy-free compound that separated from the liquors after the estimations was converted into the chloride (by treatment with precipitated silver chloride in alcoholic hydrochloric acid solution), the product was found to be identical in properties and composition with *cyanidin chloride*.

When peonidin chloride was subjected to decomposition by the action of caustic potash it was not possible to find any evidence of the production of a methyl ether of phloroglucinol, despite the fact that the reaction was carried out under very mild conditions, the only phenolic product present being phloroglucinol itself. On the other hand, by carefully regulating the conditions, an acid decomposition product was obtained that contained a methoxy group, though in the circumstances a large proportion was demethylated. Thus at 180—185° C. the acid product showed 8 per cent. MeO, at 215° only 3·5 per cent. MeO, and at 235° no MeO remained attached to the hydroxycarboxylic acid.

Peonidin sulphate is deposited as brown-red needles when a solution of the chloride in warm dilute (e.g. 7 per cent.) sulphuric acid is allowed to cool.

Diglucoside of Peonidin.

Peonin.

Peonin, the pigment of the deep violet-red peony, in which it occurs to the extent of 3—3½ per cent. of the dry weight of the petals, has been investigated by Willstätter and Nolan (Annalen, 1915, 408, 136), who obtained it, as chloride, in a beautifully crystalline condition.

For the isolation of the colouring matter the commercial, powdered, dry petals were mixed with 2 per cent. methyl alcoholic hydrochloric acid (2 litres for 1 kg. petals), the solution after standing for two hours being filtered and the residue on the filter washed with ½ per cent. methyl alcoholic acid (1½ litres). To purify it, the syrup thus obtained was mixed with methyl alcoholic hydrochloric acid (300 c.c. containing 2·2 gr. HCl), stirred, and glacial acetic acid added (210 c.c.), the mixture being then allowed to stand for sixty hours, when the syrup had been converted into a powder. This was washed with 2 per cent. methyl alcoholic hydrochloric acid, then ethyl alcohol (containing a very small per cent. HCl), and dried.

Many of the impurities present in the crude pigment were thereby rendered soluble, either by hydrolysis or acetylation, and were thus removed from the more insoluble colouring matter. The powder was further purified by repeated boiling (10 mins.) with 2 per cent. methyl alcoholic hydrochloric acid (twice with 150 c.c., followed by twice with 100 c.c.). Although some of the pigment passed into the filtrates, from which a portion only could be recovered, the bulk remained undissolved, and this was dissolved in boiling N/2HCl (800 c.c.), filtered, and the solution allowed to stand, when beautiful brown-red needles separated (6 gr.).

Peonin chloride, $C_{28}H_{33}O_{16}Cl$, readily crystallises from dilute hydrochloric acid (N/2) in the form of glistening brown-red needles (red-violet under microscope) which have the formula

$$C_{28}H_{33}O_{16}Cl,\ 5H_2O$$

It melts, with decomposition, at 165° C. The hydrate loses most of its water of crystallisation in a vacuum desiccator at room temperature, and all when dried in high vacuum at 100° C.

The salt is very easily soluble in cold water, and the aqueous solutions very readily decolorise on account of pseudo-base formation; it is somewhat less soluble in absolute alcohol, the solutions in which also show decolorisation; it is insoluble in acetone. In cold dilute hydrochloric acid it is difficultly soluble—1 litre of 1 per cent. HCl dissolves 0·11 gr. at 20° C.—whilst it is insoluble in cold, but easily soluble in hot 2N/HCl. In 7 per cent. sulphuric acid it is less soluble than is cyanin chloride, and a solution of 7 mg. in 25 c.c. rapidly deposits the greater part of the pigment in a crystalline form.

Peonin chloride closely resembles cyanin chloride in many of its reactions; pseudo-base formation proceeds with the same velocity in each case; sodium carbonate produces a pure blue colour when added to an acid solution; sodium acetate forms a fine violet, whilst caustic soda gives a blue that changes to green on standing. The ferric chloride reaction of peonin chloride is however quite different from that given by cyanin chloride, as but little colour change occurs when the reagent is added to an alcoholic solution of peonin chloride, though on addition of water a violet colour appears. The two colouring matters differ also in their solubility in water and in alcohol, and in the colour of their solutions in alcohol, peonin chloride being more red than cyanin chloride.

On hydrolysis the salt yields *peonidin chloride* (1 mol.) and

glucose (2 mols.), and, like cyanin chloride, it is optically active. The following data have been recorded by Willstätter and Nolan :—

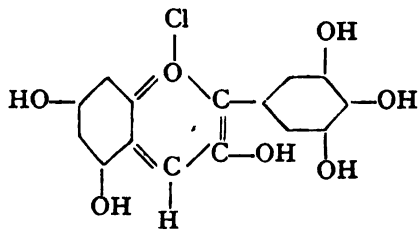
Solution in 0·05 per cent. HCl, white light as for cyanin chloride $[\alpha] = -191^\circ (\pm 5^\circ)$.

Peonin picrate may be prepared by the addition of an aqueous solution of picric acid to a suspension of the chloride in water. The chloride first dissolves, and, on standing, the picrate crystallises out in the form of red-brown (under the microscope red-violet) needles.

Delphinidin and its Derivatives.

Glucosides of delphinidin have been isolated from various kinds of grapes, from the berries of *Ampelopsis*, of *Vitis riparia*, and of the bilberry (*Vaccinium myrtillus*, Linn.), also from the flowers of the hollyhock (*Althae rosea*), delphinium (*Delphinium consolida*, Linn.), petunia (*Petunia hybrida hort.*), wild mallow (*Malva silvestris*, Linn.), and viola (*Viola tricolor*), but it is of interest to note that except in the case of the colouring matters of the delphinium and viola, all the pigments are glucosides of mono- or dimethyl ethers of delphinidin, and not of free delphinidin.

Delphinidin has been isolated in the form of its crystalline picrate, iodide, sulphate, and chloride, most frequently as chloride, and also as the colourless pseudo-base. The chloride has been obtained in no less than four distinct hydrated forms containing $1H_2O$, $1\frac{1}{2}H_2O$, $2H_2O$, and $4H_2O$ respectively. The anhydrous chloride has been shown to possess the structure—



Delphinidin chloride has been prepared by Willstätter and his collaborators by the hydrolysis of delphinin and violanin. For this purpose these glucosides were first dissolved in hot dilute hydrochloric acid (0·4 gr. in 10 c.c. of 0·5 per cent. HCl), the solution when boiling mixed with concentrated hydrochloric acid (12 c.c.) and the mixture boiled for two minutes. On cooling in contact with ice, the chloride separated, and was purified by recrystallisation. This process, which differs somewhat from that used for the preparation of pelargonidin and cyanidin from their glucosides, was adopted

to avoid a too prolonged action of the acid, whereby amorphous decomposition products are formed. Willstätter and Weil also prepared this compound by first forming the iodide by boiling with hydriodic acid as if for a Zeisel estimation, followed by conversion of that salt into the chloride by means of silver chloride in alcohol. It has also been obtained from the mono- and dimethyl ethers of delphinidin, resulting from the hydrolysis of their naturally occurring glucosides, by converting the delphinidin iodide, resulting from the Zeisel methoxy determinations of these, into the chloride as stated above.

A solution of the chloride in water readily passes through the violet colour base to the pseudo-base, a change that also takes place when warm water is added to an alcoholic solution of the chloride. A concentrated aqueous solution soon deposits the colour base as a flocculent violet precipitate.

Delphinidin chloride is easily soluble in methyl or ethyl alcohol, giving beautiful purple-coloured solutions; it is fairly soluble in amyl alcohol and passes completely from aqueous acid into amyl alcohol; it passes appreciably from an aqueous solution—less so from dilute acid solution—into ethyl acetate, and even ether will take a small fraction from an aqueous solution—particularly on addition of calcium carbonate—but dilute acid removes all from the ether.

Anhydrous delphinidin chloride does not melt below 350° C.

Willstätter and Weil describe the preparation and properties of the various hydrates of delphinidin chloride, viz. :—

$C_{15}H_{11}O_7Cl$, H_2O.—This hydrate was formerly obtained by allowing a solution of the pigment in dilute hydrochloric acid to stand over concentrated hydrochloric acid, when as the acid became gradually concentrated, crystals of the compound were deposited. As this hydrate separated when the concentration was about 3·4 per cent. HCl, and even at 5 per cent. HCl a totally different hydrate commenced to separate, it was difficult to obtain a pure product in this way. Regular yields of pure product were obtained by dissolving 0·4 gr. of the pigment in 5 c.c. of 0·5 per cent. HCl, adding 1 c.c. of 20 per cent. HCl, and keeping for several days in a closed vessel—to prevent evaporation, hence concentration—in an ice room. The crystals thus produced were homogeneous, thin, sharply cut rhombic tablets of a deep violet colour; they lose all their water of crystallisation on drying in a vacuum desiccator at room temperature, and reabsorb the same amount on standing in the air. In 0·5 per cent. HCl the compound is very easily soluble, in 3—5 per cent. still easily soluble. An interesting change occurs when it is added

to 5 per cent. HCl—at first the solid readily dissolves, producing dark streaks in the liquid, soon, however, the liquid gets lighter, then no further solid dissolves and the liquid deposits fine brown needle-like crystals, and, in about half an hour, the liquid becomes colourless. The undissolved solid gradually changes in appearance and finally consists of jagged crystals resembling aggregates of thin prisms. A very similar transformation takes place when sulphuric acid is used, the compound first dissolving, and then being redeposited in the form of fine prisms.

$C_{15}H_{11}O_7Cl$, $1\frac{1}{2}H_2O$ separates from hydrochloric acid of more than 20 per cent. concentration, and may be prepared by dissolving 0·4 gr. of pigment in 10 c.c. water, and adding 15 c.c. of concentrated hydrochloric acid—all at once—whereupon an amorphous precipitate separates, which changes in the course of a few hours into small crystals. This hydrate loses all its water when dried in a vacuum desiccator at room temperature.

$C_{15}H_{11}O_7Cl$, $2H_2O$ is the hydrate that separates on adding aqueous acid (7 per cent. to 20 per cent. HCl) to an alcoholic solution of the pigment, and allowing the alcohol to evaporate. It forms aggregates of prismatic tablets which are difficultly soluble in 5 per cent. HCl, fairly soluble in hot but insoluble in cold 7 per cent. sulphuric acid. These lose all their water of crystallisation when dried in vacuum desiccator, and the product reabsorbs water when left in the air.

$C_{15}H_{11}O_7Cl \cdot 4H_2O$ separates from 5 per cent. hydrochloric acid and is conveniently obtained by dissolving 0·3 gr. of the pigment in 5 c.c. of 0·5 per cent. HCl and adding 1·5 c.c. of 20 per cent. HCl. Crystallisation commences after standing a few hours, and practically all the pigment separates in the form of fine prisms and needles which form a chocolate-brown mass with bronze reflex, which, on account of its woolly nature, is difficult to powder. The compound loses all of its water on drying in vacuum desiccator at room temperature.

Note.—As distinct from these hydrates, Willstätter and Mieg previously described crystals of delphinidin chloride which lost 4·6 per cent. water in vacuum desiccator, and a further 4·5 per cent. in high vacuum at 105° C. Willstätter and Weil state that this is not incorrect, as crystals are indeed frequently met with that do behave thus, but that they have not been able to ascertain the conditions necessary for their formation. Crystals that behave thus are usually needle-like in form.

Willstätter and Mieg record the following reactions of delphinidin

chloride: An acidified solution on addition of sodium carbonate gives a violet, then blue coloration which is unstable; lead acetate produces a blue precipitate; sodium bisulphite forms a colourless, soluble product that is decomposed by dilute hydrochloric acid with liberation of the pigment; ferric chloride, on addition to an alcoholic solution, gives a fine intense and stable blue coloration, but on dilution with water this changes to an unstable violet; Fehling's solution is vigorously reduced, even when cold.

Zeisel estimations proved the absence of methoxy groups in the compound. When decomposed by means of 75 per cent. caustic potash at 250° C., delphinidin chloride is stated to yield *phloroglucinol* and *pyrogallol*, together with a small amount of *gallic acid*, but owing to the small quantities available, Willstätter and Mieg state that the identification of these products is incomplete.

The absorption spectrum of delphinidin chloride is described as consisting of one band in the yellow and green, which is fairly well defined, more so when long columns are examined than when shorter ones are used. The data given are:—

Solution in ethyl alcohol, 1 mol. in 2500 litres—

Column 2·5 mm.	595 . . 590 –	– 529 . 512
„ 5·0 „	603 . . 598 – 500 . .	493

Solution in ethyl alcohol, 1 mol. in 12,500 litres—

Column 2·5 mm.	581 . . 546	
„ 5·0 „	587 . . 582 . . .	550 . 533

Delphinidin sulphate separates in the form of characteristic long prisms when solutions of the pigment in hot dilute sulphuric acid are allowed to cool.

Delphinidin iodide is deposited from a boiling mixture of phenol and hydriodic acid as brown glistening prisms and pointed leaflets. By solution in acidified alcohol and treatment with precipitated silver chloride and a trace of silver, it is converted into delphinidin chloride.

Delphinidin picrate crystallises in fine red-brown needles and prisms, and is difficultly soluble in water.

Delphinidin pseudo-base, $C_{15}H_{12}O_8$.—This compound, which is characterised by considerable crystallising power, was prepared by Willstätter and Mieg in the following way: 1 gr. of delphinidin chloride was warmed rapidly with ½ litre of water to the temperature of the water-bath. After quarter of an hour—when the liquid had already become much lighter—2 gr. sodium phosphate (primary) were

added and this brought the change rapidly to completion. The solution was cooled, saturated with ammonium sulphate, and extracted with ether; the ether extract, which contained a small quantity of unchanged substance, was washed with a few c.c. of dilute hydrochloric acid, then with water, dried over sodium sulphate, and evaporated *in vacuo*. The product thus obtained was slightly brownish in colour, but was readily recrystallised from ether, or from water, when the base separated in the form of colourless prisms. The substance must be protected from acid fumes, or from glass vessels possessing an alkaline reaction.

When heated to 120—130° C. the substance is rapidly coloured violet, whereas at higher temperatures it becomes darker and gradually sinters. It is easily soluble in ethyl alcohol, acetone, ethyl acetate, and glacial acetic acid; in ether it is somewhat more difficultly soluble, and insoluble in benzol; from solutions in glacial acetic acid, fine needle-like crystals separate on the addition of toluol. This pseudo-base is stable when in dry crystalline form, also in dilute aqueous, or ether, solution; in aqueous sodium carbonate it dissolves with a yellow colour, which is fairly stable. Mineral acids convert it into the coloured salt, a solution in cold 7 per cent. hydrochloric acid becoming intensely red in a few hours, whereas, if boiled, this change occurs in a few minutes.

Derivatives of Delphinidin.

Monomethyl ethers, and their glucosides, see p. 315.
Dimethyl ethers, and their glucosides, see p. 327.
Disaccharides of delphinidin: violanin and delphinin.

Rhamnoglucoside.

Violanin.

Violanin, the colouring matter of the blue-black pansy (*Viola tricolor*), has been isolated and examined by Willstätter and Weil (Annalen, 1916, 412, 178), whose investigations are, however, as yet incomplete. The petals used contained as much as 24 per cent. of their dry weight of violanin, being the richest in colour content of all the flowers of the anthocyan pigments which have as yet been examined. In order to prepare it the fresh petals were employed. Although glacial acetic acid was first used for extraction, it was found that 2 per cent. methyl alcoholic hydrochloric acid gave the best results, both as to completeness of extraction and purity of the crude product obtained. The petals (100 gr.) were extracted with

this medium (1 litre), filtered after standing two hours, the residue washed with a smaller quantity (100 c.c.) of the solvent, and the filtrate mixed with two and a half times its volume of ether, whereby the pigment was precipitated as chloride (4—5 gr.). By dissolving (10 gr.) this in 0·01 per cent. hydrochloric acid (250 c.c.), adding alcohol (100 c.c.), then 4 per cent. hydrochloric acid (250 c.c.), and allowing to stand for several days in covered vessels, the salt crystallised out, and when purified formed six-sided, or tetrahedral tablets of a blue-violet colour, having a greenish metallic lustre. It is stated that in the recrystallisation, acetone can, with advantage, replace the alcohol. Violanin has also been isolated by Everest (Proc. Royal Soc., 1918, B) from dried purple-black violas (Sutton's " Black Knight "), and evidence was obtained that a glucoside of myricetin is also present in these flowers.

Violanin chloride, ($C_{27}H_{31}O_{16}Cl$?), as crystalline hydrate, loses about 15—16 per cent. of water (= $6H_2O$) when dried in a vacuum desiccator, and a further 2·5 per cent. in high vacuum at 105° C. When completely dehydrated it loses hydrochloric acid, as is the case also with delphinidin and petunidin chlorides, and although Willstätter and Weil—following their usual practice in such cases—calculated their analytical figures to the chlorine-free base in order to eliminate this difficulty, their results were not in satisfactory agreement with the formula $C_{27}H_{30}O_{16}$, which corresponds to that of simple rhamnoglucoside of delphinidin. Moreover, although they were able to show that on hydrolysis violanin chloride yielded *delphinidin chloride* (1 molecule), *rhamnose*, and *glucose*, they were not able to obtain figures sufficiently in agreement with the presence of 1 molecule each of the sugars, to satisfactorily settle the composition of this pigment. In view of the low rhamnose content found when estimated by Tollens' method, the pigment was carefully fractionally extracted from an aqueous acid solution by amyl alcohol, to find whether there was a mixture of rhamnoglucoside and diglucoside present, but the results proved that the substance was homogeneous.

Solutions of violanin chloride are bluer than those of malvin chloride, and closely resemble those of delphinin chloride, but they show decolorisation with formation of pseudo-base, which does not occur with solutions of delphinin chloride. Its solutions in water are bluish-red; in alcohol violet-red.

This salt is very soluble in acidified methyl alcohol, only fairly so in ethyl alcohol; in water it is difficultly soluble; in 0·15 per cent. hydrochloric acid it is very easily soluble, in 0·5 per cent. still fairly

so, but as the per cent. of HCl increases, the solubility decreases, till in 1 per cent. HCl it is only little soluble, and in 5—12 per cent. almost insoluble. Curiously enough in 20 per cent. it is again appreciably soluble, and is easily so in concentrated hydrochloric acid. In dilute sulphuric acid (0·05—7 per cent. and higher) it is practically insoluble, and a warm, saturated solution deposits the colouring matter completely on cooling.

An acid solution turns blue when sodium carbonate, or caustic soda, is added, and its solution in aqueous sodium phosphate (ordinary) is likewise blue. When ferric chloride is added to an ethyl alcoholic solution, it gives a blue coloration.

Violanin chloride, like the rhamnoglucoside anthocyans, keracyanin and prunicyanin, behaves, in regard to distribution between amyl alcohol and dilute acid, very much more like a normal monoglucoside than as a diglucoside, and it is stated to have a distribution number approximating to that of a normal monoglucoside. That this is not due to admixture of monoglucoside was shown by Willstätter and Weil by fractional extraction with amyl alcohol, and quantitative hydrolysis of the fractions of the pigment thus obtained.

Violanin picrate has been prepared by dissolving violanin chloride in ten times its weight of hot 0·01 per cent. hydrochloric acid, and adding to the solution finely divided picric acid. On cooling, a mass of fine cherry-red needles separates, which, when dry, forms a copper-red mass. The picrate is fairly soluble in water.

Complex Diglucoside.

Delphinin.

Delphinin, the pigment of wild purple delphinium (*Delphinium consolida*, Linn.), has been investigated by Willstätter and Mieg (Annalen, 1915, 408, 61). It is present in the flowers to the extent of about 1¾ per cent. of the dry weight, and it has been shown that it occurs as the free colouring matter, neither combined with alkalis as a salt, nor with acids as an oxonium compound. It is very interesting to note that delphinin differs from all the other anthocyanins that have yet been isolated, in that dilute neutral solutions of its salts, or of the free base, have never been observed to pass to the pseudo-base, and it is this stability of the colour base that made it possible for Willstätter and Mieg to isolate it from the flower petals without the use of any chemical reagents, alcohol alone of various concentrations serving this purpose. The process was long and tedious,

but consisted in the main of repeated solution of the crude pigment in alcohol of such a concentration that a certain portion of the impurities remain insoluble, separation of these from the liquor—usually by means of a Jouan "Bol" centrifuge* — and reprecipitation of the colour by increasing the concentration of the alcohol. After use had been made of this, the pigment was sufficiently insoluble in water to allow of its treatment for the removal of impurity. Their final product was free from acid and almost free from ash (0·5 per cent. ash, as sulphate), and hence was either the colour base, or an internal salt of it.

Delphinin was, however, best isolated as the chloride. The colouring matter, after one precipitation from dilute alcohol, followed by one purification with water, was dissolved in twenty times its weight of 0·2 per cent. hydrochloric acid, the solution filtered, and 20 per cent. hydrochloric acid added, when the chloride separated out in a sufficiently pure condition for crystallisation. It is stated that an alternative method—working as chloride from the start—is more convenient and rapid; the petals being extracted with ethyl alcoholic hydrochloric acid—3 kg. with 10 litres of solvent (7·5 litres of 96 per cent. EtOH, 1·5 litres conc. HCl, and 1 litre of water) (as this caused no swelling of the dry petal powder, much larger batches could be worked than when dilute alcohol was used for extraction, and again filtration was possible without the addition of sand)—and the residue after filtration washed with 3 litres of the same solvent. The intense red extract (9 litres), when mixed with an equal volume of ether, deposited the pigment as a syrup which, after decantation of the liquors, was rubbed with alcohol to dehydrate it, then dissolved in methyl alcohol (1·5 litres), and the pigment precipitated as a powder by the addition of absolute alcohol (3 litres) and ether (2 litres). The product was redissolved in methyl alcohol (1 litre), filtered, and reprecipitated by the addition of absolute alcohol (1½ litres) and ether. After drying the substance was dissolved in hot 2 per cent. hydrochloric acid (250 c.c.), warmed for half an hour on the water-bath, cooled, and the colouring matter precipitated by the addition of 10 per cent. hydrochloric acid (1·3 litres). Following upon this purification, it was redissolved in cold methyl alcohol (400 c.c.) and reprecipitated by addition of absolute alcohol (½ litre) and ether (several times its volume).

* The use of this machine for this purpose in connection with the anthocyans was introduced by Willstätter and Everest, who employed it for the repeated fractionation of the blue corn-flower pigment. It is very doubtful whether without its use their work could have been brought to a successful conclusion.

The product obtained by either of the above processes was crystallised by adding the finely powdered pure amorphous product (6 gr. to 400 c.c.) to 3 per cent. hydrochloric acid and warming in an open beaker, with frequent stirring, for 1½ hours, when it was completely converted into crystalline aggregates consisting of tablets and prisms, which were collected, washed with 3 per cent. hydrochloric acid, and dried. If larger volumes of hydrochloric acid were used, the size of crystal was larger, but the yield was decreased. In the best cases, about 70 per cent. of the weight of the product taken was thus obtained in the crystalline form.

Delphinin chloride, $C_{41}H_{39}O_{21}Cl$, as crystalline hydrate appears to contain 12 molecules of water, and on drying in high vacuum at 130° C. passes to a product for which the composition

$$C_{41}H_{39}O_{21}Cl, 2H_2O$$

is given, but owing to the fact that some hydrochloric acid was lost on drying, the analytical figures had to be calculated to the acid-free product. It was not found possible to remove the water thus assumed to remain attached to the molecule. The crystalline substance ($12H_2O$) consists of prismatic tablets of deep brown-red colour (by transmitted light under microscope bluish-red), having a surface shimmer (*mattem Samtglanz*); the crystals are soft, and mark paper cherry-red. The dried product ($2H_2O$), when heated, commences to sinter at 150—160° C., and melts with much decomposition and swelling at 200—203° C.

On adding water to the crystalline chloride it is immediately converted, by hydrolytic dissociation, into the colour base, which separates in the form of deep violet flakes. Formation of the colourless pseudo-base has never been observed with solutions of delphinin, or of its salts.

The chloride is fairly easily soluble in cold methyl alcohol, but difficultly soluble in absolute ethyl alcohol, even when warm; the alcoholic solutions are intense red, with bluish tinge, and solutions in fairly dilute ethyl alcohol (e.g. 50 per cent.) become much more blue when heated, returning to their original colour when cooled. It is insoluble in amyl alcohol, and is easily soluble in cold hydrochloric acid, up to 0·5 per cent. HCl, but only soluble in hot acid containing 1—2 per cent. HCl. In dilute sulphuric acid it is very little soluble (concentrations varying from 0·03—7 per cent.), but in concentrated sulphuric acid it is readily soluble forming an orange-red solution.

Acid solutions of the chloride are bluer than similar solutions

of oenin, myrtillin, and althein chlorides, and are much more intense in colour than corresponding solutions of cyanin chloride.

When sodium carbonate is added to an acid solution of delphinin chloride it produces a deep blue coloration, which is stable for hours in the cold, and in absence of excess of alkali, but on warming passes through green to yellow, whereas caustic soda produces the same changes, but more rapidly. Acidification of the yellow solution does not reproduce the anthocyan. Lead acetate gives an indigo-blue coloured flocculent precipitate when added to a solution of the salt; alcoholic or aqueous ferric chloride an intense blue solution, and sodium bisulphite forms a very soluble colourless compound, which is decomposed by acids with reproduction of the pigment. Fehling's solution is noticeably reduced if hot.

Delphinin chloride is optically active, and Willstätter and Mieg record the following measurements :—

White light (½ watt Osram lamp 20 cms. distant). Solution in 1 per cent. HCl, 1 dcm. tube $[\alpha] = -1231°$; ½ dcm. tube $[\alpha] = -1439°$; mono-chromatic light (solutions used above had to be diluted to four times its original volume)

$$[\alpha]_c = -1364° (\pm 150°); \quad [\alpha]_{614} = -2273° (\pm 150°).$$

The absorption spectrum is described by the same authors as consisting of one band that ends very indistinctly, and which differs from that of cyanin chloride in that it does not reach the blue region. The data given are: Solution in 0·25 per cent. HCl, 1 mol. in 2500 litres—

Column 2·5 mm. 575 . 538 – – 515 . 495
„ 5·0 „ 586 . . . 545 – 512 . 490

Delphinin chloride is only slowly hydrolysed by boiling dilute hydrochloric acid, but rapidly by 20 per cent. acid, and in view of the fact that the acid, beyond causing hydrolysis, gives rise to amorphous products, it is advantageous that the operation be carried through as rapidly as possible (3 mins.) and the mixture cooled at once. The products of hydrolysis are *delphinidin chloride* (1 mol.), *glucose* (2 mols.), and *p-hydroxy benzoic acid* (2 mols.). In order to confirm this result and to see whether the *p*-hydroxy benzoic acid was a regular constituent of the pigment, the flowers from several sources, and three different harvests, 1911—1913, were examined by these authors, and in every case the same result was obtained. Willstätter and Mieg express the opinion that the *p*-hydroxy benzoic acid in delphinin is attached

to the glucose molecules, and not to the phenolic hydroxyl groups of the pigment complex.

The distribution number of delphinin resembles that of a normal diglucoside.

Delphinin colour base is readily produced by adding water to the chloride, and thus separates as a deep violet flocculent precipitate. It is difficultly soluble in boiling methyl alcohol, and insoluble in ethyl alcohol, but dissolves in very dilute ethyl alcohol, or acetone, forming blue-violet solutions. When a solution in dilute alcohol is kept under a bell-jar over absolute alcohol, whereby the alcohol concentration slowly increases, the colour base is deposited in the form of rosettes of microscopic violet coloured needles.

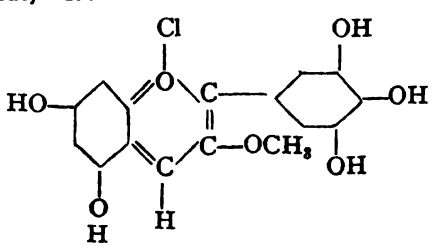
Delphinin picrate, a difficultly soluble compound, was prepared as a brown-red flocculent precipitate by Willstätter and Mieg, but was not obtained in a crystalline condition.

The Methyl Ethers of Delphinidin.

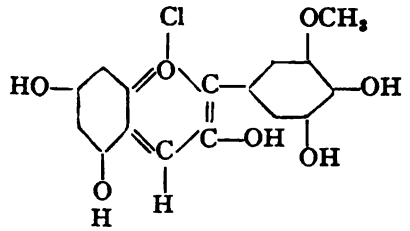
The investigations of Willstätter and his collaborators have thus far resulted in the isolation of three monomethyl ethers—possibly a fourth—and two dimethyl ethers of delphinidin, together with the glucosides derived from them. The monomethyl ethers have been designated *ampelopsidin*, *myrtillidin* and *petunidin*, being, respectively, the products of hydrolysis of the glucosidal pigments of the fruits of *Ampelopsis quinquefolia*, Michx. (*Vitis hederacea*, Ehrh.), and bilberry (*Vaccinium myrtillus*, Linn.), and of the flowers of the petunia, whilst the product similarly obtained from the fruit of *Vitis riparia*, Michx. (*odoratissima*, J. Don) is either a fourth monomethyl ether, or is identical with myrtillidin, the evidence available being insufficient for a final decision. The dimethyl ethers are known as *malvidin* and *oenidin*, and have been obtained from the violet flowers of the wild mallow (*Malva silvestris*, Linn.) and the fruit of the black North Italian grape respectively.

There are five possible formulæ for the monomethyl ethers of delphinidin chloride, viz. :—

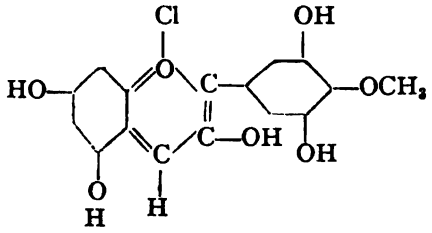
(I)



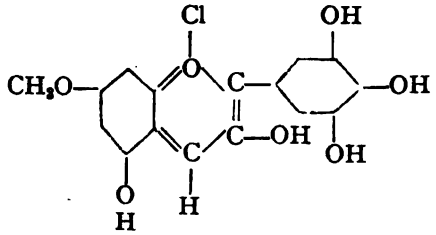
(2)



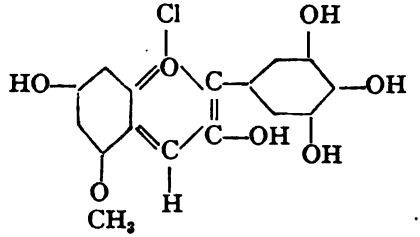
(3)



(4)



(5)

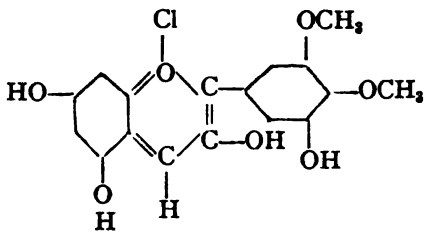


and it has been possible to assign, with some degree of certainty, the formulæ (1), (2), and (3) to compounds that have been already isolated. In this connection the chief evidence utilised has consisted of the presence, or absence, of a methoxy group in one or other of the products of alkaline decomposition—e.g. whilst neither myrtillidin nor petunidin yields a methyl ether of phloroglucinol, the methoxy group can be detected in the acid product from the other half of the structure. Further, the examination of the behaviour of the various compounds with ferric chloride has proved of importance.

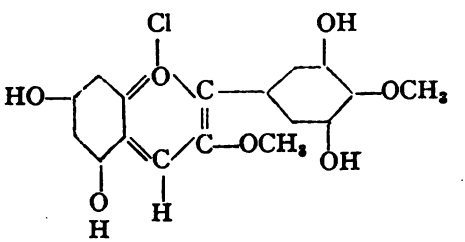
In such a way formulæ (1) and (2) have been given, at least tentatively, to myrtillidin and petunidin chlorides (though it has not been possible to state which is applicable to either), and formula (3) to ampelopsidin. This latter suggestion is interesting in view of the fact that alkali decomposition of the compound has not been carried out, but, as the salt shows but a very weak ferric chloride reaction, there is reason to assume that (3) represents this monomethyl ether of delphinidin. The anthocyanidin from *Vitis riparia*, which possesses very strong ferric chloride reaction, will, if it proves to be different from myrtillidin, be represented either by (4) or (5).

Theoretically, there are eleven possible dimethyl ethers of delphinidin, but, thus far, only two have been isolated, viz. oenidin and malvidin. To these the respective formulæ (1) or (2), and (3) or (4), have been given tentatively by Willstätter and his collaborators—

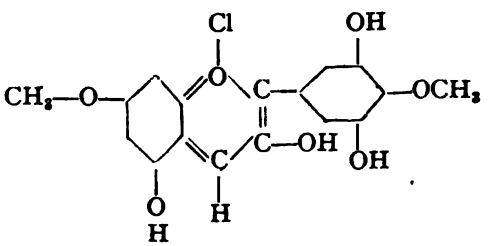
(1)



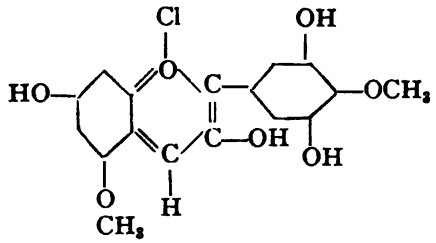
(2)



(3)



(4)

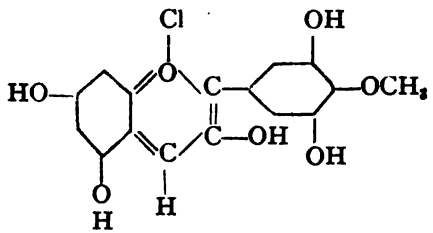


The analytical data point very strongly to the presence of small amounts of dimethyl ethers in most of the monomethyl ethers, as at present purified, and of some monomethyl ether in the dimethyl ether-oenidin, but, on the other hand, petunidin and malvidin give figures that point to their being pure substances. The monomethyl ether presumed to be present mixed with oenidin is apparently ampelopsidin.

DELPHINIDIN MONOMETHYL ETHERS AND THEIR DERIVATIVES.

AMPELOPSIDIN.

Ampelopsidin chloride, $C_{16}H_{13}O_7Cl$, has been prepared by Willstätter and Zollinger (Annalen, 1916, 412, 216), by hydrolysis of its glucoside ampelopsin, and to it they tentatively ascribe the following structure:—



It forms a crystalline hydrate which separates in prisms, but the specimens prepared contained varying amounts of water of crystallisation. It is very easily soluble in 1 per cent. hydrochloric acid, easily so in 3 per cent., but difficultly soluble in 5 per cent. acid; in 7 per cent. sulphuric acid it is easily soluble. When ferric chloride is added to an alcoholic solution, a violet-blue coloration is produced, whilst, in aqueous solution, the colour is red-violet. In neither case is the colour of great intensity, and in this respect, this substance differs from myrtillidin, petunidin, and the anthocyanidin from *Vitis riparia*. Zeisel estimations give values that are rather high for the

presence of one methoxy group in the molecule. The examination of ampelopsidin chloride has not yet been completed.

AMPELOPSIN.

Ampelopsin—monoglucoside of ampelopsidin—is the pigment of the berries of *Ampelopsis quinquefolia*, Michx. (*Vitis hederacea*, Ehrh.), and has been isolated and partially examined by Willstätter and Zollinger.

Although the pigment permeates the whole fruit, it is most concentrated in the skins, and these only were used for the extraction, which was carried out with glacial acetic acid. After precipitating the extract by means of ether, the moist precipitate was dissolved in methyl alcoholic hydrochloric acid, and reprecipitated with ether, this treatment being followed by solution in hot 0·1 per cent. hydrochloric acid, and formation of the picrate by adding powdered picric acid to the filtered liquid.

This conversion was performed rapidly, and with small quantities, and the solution when cooled deposited the picrate in the crystalline condition as carmine-red needles. When this product was dissolved in 3—4 per cent. methyl alcoholic hydrochloric acid, and ether added, ampelopsidin chloride separated in an amorphous form, but, when this was dissolved in aqueous alcoholic hydrochloric acid (20 parts water, 10 of ethyl alcohol, and 7 of 25 per cent. HCl), and after several days the concentration of the alcohol increased, the chloride separated in long thin prisms having a brown-green reflex.*

Ampelopsin chloride, $C_{22}H_{23}O_{12}Cl$, forms a crystalline hydrate, which has the composition $C_{22}H_{23}O_{12}Cl, 4H_2O$.

The chloride is easily soluble in acidified methyl or ethyl alcohol, and resembles oenin in its solubility in dilute acids.

When an acid solution is treated with sodium carbonate, a stable blue-violet to violet coloration (depending upon the concentration of the solution) is produced, whilst caustic soda gives a fairly stable blue colour (difference from myrtillin). Ferric chloride produces a weak colour reaction (violet) in aqueous solution, and a good violet in alcoholic solution (difference from myrtillin and petunin chlorides and *Vitis riparia* pigment).

* Willstätter and Zollinger mention that this crystallisation process may cause the production of a monoglucoside from a diglucoside, but it would appear that tests of the distribution number before and after crystallisation should settle this point—which is important as regards our knowledge of the actual condition of the natural pigment.

The distribution number is 9·8, hence is that of a normal monoglucoside anthocyan, and hydrolysis of the salt produced *ampelopsidin chloride* (1 mol.) and *glucose* (1 mol.). Zeisel estimations showed the presence of a methoxy group, but the figures obtained—like those for the non-glucoside—were high, and suggest the presence of a dimethyl ether as impurity.

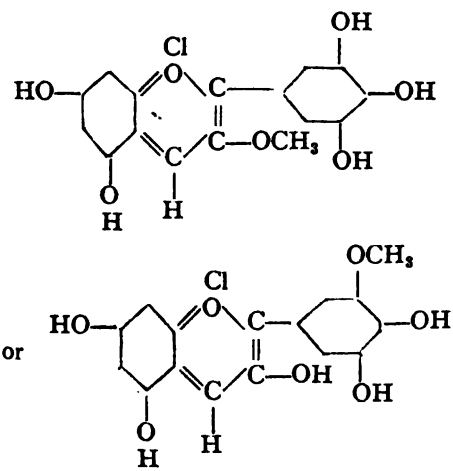
MYRTILLIDIN.

Myrtillidin has been isolated in the form of its crystalline chloride, by hydrolysis of its monosaccharides myrtillin and althein, in the former of which it occurs combined with galactose, and in the latter with glucose.

Myrtillidin chloride crystallises in clusters of deep brown prisms which have a fine greenish reflex, or (from 3 per cent. HCl) in red-brown blunt prismatic tablets, which have the composition—

$$C_{16}H_{13}O_7Cl,\ 1\tfrac{1}{2}H_2O$$

On drying, like several similar compounds, it loses a portion of its hydrochloric acid, but, by calculating their analytical figures to the chlorine-free base, Willstätter and Zollinger obtained values in agreement with $C_{16}H_{12}O_7$, which corresponded to an anhydrous chloride $C_{16}H_{13}O_7Cl$. Estimations of the methoxy group showed that one such group was present in the molecule. The chloride probably has the structure—



or

It has been shown that the methoxy group is not present in the portion of the molecule that yields phloroglucinol when the pigment is melted with alkali, and the intense character of its

reaction with ferric chloride is in harmony with either of the above formulæ.

Myrtillidin chloride, deposited from methyl alcoholic-aqueous hydrochloric acid, and washed with alcohol, is insoluble in cold 3 per cent. hydrochloric acid, but very easily soluble in 0·5 per cent., but, after standing in the air, it becomes appreciably soluble in 3 per cent. HCl also (difference from petunidin). If, after washing with alcohol, the chloride is dissolved in hot ½ per cent. HCl and precipitated by addition of an equal volume of concentrated HCl, the product is also appreciably soluble in 3 per cent. HCl (petunidin chloride similarly prepared is insoluble).

The salt is very easily soluble in ethyl alcohol, and on adding ferric chloride to the alcoholic solution, an intense blue coloration is produced. When myrtillidin chloride is demethylated, it yields *delphinidin.*

Willstätter and Zollinger describe the absorption spectrum of this salt in alcoholic solution as consisting of one band which passes rather more into the orange than does that of oenidin, and has very ill-defined edges. For a solution of 0·007 gr. in 50 c.c. alcohol they recorded the following measurements:—

Column	2·5 mm.	596 . . 591 – 575 – – 513 . 501
„	5·0 „	604 . . 599 – 493 . . . 487/455
„	10·0 „	609 . . 605 – 478 . . . to end of visible.

MYRTILLIN.

Myrtillin—a monoglucoside of myrtillidin—the pigment of the fruit of the bilberry (*Vaccinium myrtillus*, Linn.), has been investigated by various workers. A. Andree (Archiv für Pharm., 1879, 13, 90) attempted to isolate the colouring matter of the bilberry, whilst Heise (Arbeits. a. d. K. Gesundht., 1894, ix., 478) prepared therefrom two coloured substances, both in an amorphous condition, one soluble in dilute acid, which he considered to be a glucoside, and a second insoluble in dilute aqueous acid, a non-glucoside, and related to the former as shown by the equation—

$$C_{20}H_{24}O_{12} + H_2O = C_6H_{12}O_6 + C_{14}H_{14}O_7$$

It remained for Willstätter and Zollinger (Annalen, 1915, 408, 83, and 1916, 412, 205) to isolate the pigment in a pure crystalline condition, and to determine its relationship to the other colouring matters of this group.

They utilised only the skins of the berries, and these, after

pressing first in a wine press and then a hydraulic press, and drying, formed 6 per cent. of the weight of the berries. The extraction was preferably carried out by means of boiling alcohol (MeOH or EtOH), containing 1 or 2 drops of alcoholic hydrochloric acid, and the extract was precipitated by ether (2—3 vols.), preferably after the addition of glacial acetic acid (2 vols.), which caused the pigment to separate as a syrup. The crude product was then purified by solution in water and reprecipitation by means of concentrated hydrochloric acid, this process being repeated and followed by solution of the product in 2 per cent. methyl alcoholic hydrochloric acid and slow fractional precipitation by standing over ether under a bell-jar, or in a desiccator. In this way the product was obtained as fine red microscopic spheres, and was recrystallised by solution in methyl alcohol, addition of aqueous hydrochloric acid, and slow evaporation of the alcohol, when the chloride separated in the form of fine bronze-brown crystals (usually three-sided or rhombic tablets) which showed a green reflex.

An alternative method of isolation involved the use of the picrate, which was prepared from the crude product by stirring this into a cold saturated solution of picric acid, when fine needles of the picrate separated. On treating this with methyl alcoholic hydrochloric acid, and precipitating with ether, the chloride was obtained. By again dissolving this in methyl alcoholic hydrochloric acid, adding concentrated acid to the solution, on standing the chloride separated in the micro-spherical condition, and could be crystallised as above stated.

Myrtillin chloride, $C_{22}H_{23}O_{12}Cl$, forms a crystalline hydrate of the composition $C_{22}H_{23}O_{12}Cl$, $4H_2O$, which loses $3\frac{1}{2}H_2O$ when dried in a vacuum desiccator, or in high vacuum at 50° C., but only gives up the last half molecule of water when dried in high vacuum at 105° C.

The chloride is very soluble in water, giving a brown-red solution, which, if dilute, becomes decolorised as the result of pseudo-base formation, a similar change occurring in dilute alcoholic solution, but more slowly. In absolute alcohol the salt is not easily soluble (difference from althein chloride), but in methyl alcohol it dissolves readily; in 7 per cent. sulphuric acid it is very easily soluble, as also in the concentrated acid; in very dilute hydrochloric acid it is easily soluble, in 5 per cent. less so, in 10 per cent. but little soluble, and in 20 per cent. almost insoluble.

When ferric chloride is added to an alcoholic solution, a fine blue colour is produced, which on dilution with water changes to

blue-violet and is fairly stable. Caustic soda when added to an acid solution gives a pure blue colour that is unstable on dilution, whereas sodium carbonate produces only a blue-violet colour which is fairly permanent in these circumstances. Neutral, or basic, lead acetate produces a deep blue flocculent precipitate, and copper sulphate a dull red deposit when added to a solution of the salt.

Willstätter and Zollinger described the absorption spectrum as consisting of a single broad band with ill-defined edges. They gave the following measurements for a solution of 0·015 gr. in 50 c.c. of 7 per cent. H_2SO_4:—

Column 2·5 mm. 559 · 552 . . . 543 – 491 . . 481
„ 5·0 „ 587 · 574 . . 564 – 455 . . . to end of visible.

The distribution number is 10·9, which is very slightly higher than that of most monoglucoside anthocyans, and hydrolysis yields myrtillidin chloride (1 mol.) and galactose (1 mol.).

Myrtillin picrate, the preparation of which is described above, is difficultly soluble and crystallises in fine red needles.

ALTHAEIN.

Althaein—a monosaccharide of myrtillidin—the colouring matter of the black malva (hollyhock) (*Althae rosea*, Cav.) has been the subject of investigation by several workers, and it would appear that some of the earliest chemical work on this pigment was encouraged by the Bavarian Government on account of the use then made of the pigment in that country for dyeing and printing (Bull. de la Soc. d'encouragement, 1860, 332; Polyt. Zentr., 1860, 1540). In 1892 R. Glan (Diss. Erlangen, 1892) isolated a colouring matter from the flowers of the black hollyhock by means of the lead salt; he considered this to be a glucoside, and by hydrolysis obtained a sugar-free product, which later he also prepared by a direct treatment of the flowers with 30 per cent. sulphuric acid. He decomposed the sugar-free compound by melting with alkali, and stated that his products were catechol and protocatechuic acid. Later Grafe (Sitzber. d. K. K. Akad. d. Wiss. Wien., 1906, 115, 975; and 1909, 118, 1033) also attempted the isolation of this colouring matter, likewise making use of the lead salt. As a result he described two pigments, one a glucoside of a dibasic acid which contained an aldehyde group and had the composition $C_{20}H_{20}O_{13}$, and the second a non-glucoside of the composition $C_{14}H_{16}O_6$, which he considered to be related to the first in the following way:—

$$C_{20}H_{20}O_{12} + H_2O = C_6H_{12}O_6 + C_{14}H_{18}O_8 \text{ (hypothetical)} *$$
$$\text{then: } 2C_{14}H_{18}O_8 - 2H_2O - O_2 = 2C_{14}H_{16}O_6.$$

By the action of melted alkali on the latter he obtained hydroquinone and catechol.

It was not, however, until Willstätter and Martin undertook the investigation of this pigment that a satisfactory chemical knowledge of its nature was gained. These authors (Annalen, 1915, 408, 100) succeeded in isolating the colouring matter, as chloride, in a pure condition, and although their investigations were incomplete, described its more important properties and identified the sugar-free pigment produced from it by hydrolysis. They found that the pigment was present in the flowers only as glucoside.

This was isolated from the dry commercial petals—"Flores malvae arboreae"—which contain about 11 per cent. of their weight of colouring matter. The best medium for extraction was cold methyl alcoholic hydrochloric acid (2 per cent. HCl), and from the extract the crude pigment was precipitated by addition of ether. The process of purification adopted by these authors is stated to be open to improvement, but the best method described consists in converting the raw product direct into the picrate, which separates in a crystalline condition, recrystallising several times from water, reconverting the picrate into chloride by means of alcoholic hydrochloric acid and converting the resulting purified chloride into a crystalline condition by dissolving it in methyl alcoholic hydrochloric acid, adding aqueous acid, and allowing the alcohol to evaporate slowly. The althaein chloride thus separated in the form of homogeneous crystals.

Althaein chloride, $C_{22}H_{23}O_{12}Cl$, forms a crystalline hydrate which separates as regular brown-red prisms with bronze reflex. The specimens obtained by Willstätter and Martin appeared to contain varying amounts of water (10—15 per cent.), whereas $C_{22}H_{23}O_{12}Cl$, $4H_2O$, requires 12·28 per cent.

The chloride is easily soluble in cold water, the solutions, which are brown-red in colour, becoming colourless if diluted as the result of pseudo-base formation. In dilute hydrochloric acid (½—2 per cent.) the salt is very soluble, in 5 per cent. still fairly soluble, but the solubility decreases as the concentration of the acid is increased. In 7 per cent. sulphuric acid it is easily soluble; in glacial acetic acid almost insoluble; in methyl alcohol the salt dissolves readily, in ethyl alcohol, less so.

* This equation of Grafe's does not balance.

In alcoholic solution, ferric chloride produces an intense violet-blue coloration, which, on dilution with water, passes to violet, and these colours are less stable than those produced with myrtillin chloride. With sodium carbonate, or with caustic soda, an acid solution gives a violet colour changing to blue.

Its distribution number resembles that of other monoglucoside anthocyans, and on hydrolysis it yields *myrtillidin* (1 mol.) and *glucose* (?) (1 mol.).

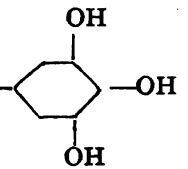
Althaein chloride is optically active, and Willstätter and Martin give the following values for a solution in 0·1 per cent. HCl :—

$$[\alpha]_{623} = -655^\circ;\ [\alpha]_C = -545^\circ;\ [\alpha]_{692} = -291^\circ.$$

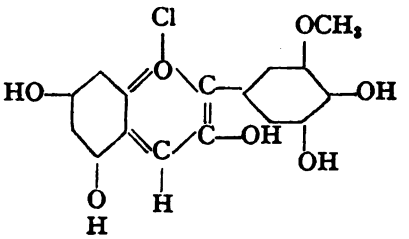
Althaein picrate is difficultly soluble, and can readily be crystallised from water.

PETUNIDIN.

Petunidin, which occurs in the form of its diglucoside, *petunin*, in the flowers of the cultivated petunia, has been prepared by Willstätter and Burdick (Annalen, 1916, 412, 217). It is a monomethyl ether of delphinidin, and resembles myrtillidin very closely. As with that compound, it was shown, by careful decomposition with alkali, that the methoxy group is attached to the acidic decomposition product, and not to the phloroglucinol nucleus. In view of the fact that petunidin, as also myrtillidin, yields an intense ferric chloride reaction, it is improbable that its methyl is attached to

the middle OH of the group 

Hence it is considered that petunidin chloride has one, myrtillidin chloride the other, of the following structures, differentiation not being possible until further data are available :—



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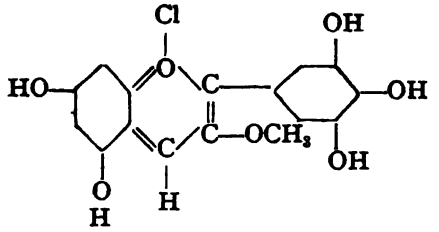


Petunidin chloride, $C_{16}H_{13}O_7Cl$, prepared by the hydrolysis of the glucoside with aqueous hydrochloric acid, did not separate in crystalline form, but was obtained so by solution in warm dilute hydrochloric acid, precipitation by the addition of concentrated acid, resolution in methyl alcohol, addition of 7 per cent. aq. HCl, and crystallisation by allowing slow evaporation to take place. If, however, petunin chloride was hydrolysed by warming with 20 per cent. ethyl alcoholic hydrochloric acid, then 3 per cent. aqueous acid added, and the alcohol allowed to evaporate, petunidin chloride separated as clusters of thin grey-brown prisms. From a solution in 0·5 per cent. hydrochloric acid, on addition of 20 per cent. acid, the chloride was deposited in the form of grey-brown pointed rhombic leaflets (under these conditions myrtillidin chloride separates as fan-like aggregates of brown-red prisms). Petunidin chloride is obtained from 3 per cent. HCl, by slow evaporation, in bundles of long thin yellow-brown prisms, whilst myrtillidin chloride forms blunt red-brown prismatic tablets. Petunidin chloride differs from myrtillidin chloride in the form of its crystals, in the composition of its hydrates, and in its solubility.

When crystallised from hydrochloric acid it has the composition $C_{16}H_{13}O_7Cl$, $2H_2O$, and most of this water is lost in a vacuum desiccator, the remainder being evolved in high vacuum at 105° C.

In the table on the next page are shown some of the differences between petunidin chloride and myrtillidin chloride to which Willstätter and Burdick have drawn attention.

Petunidin chloride is very easily soluble in ethyl alcohol. As isolated from methyl alcoholic-aqueous hydrochloric acid it is easily soluble in ½—1 per cent. hydrochloric acid, and appreciably soluble in 3 per cent. acid, but on standing this solution redeposits the salt.

Zeisel estimations showed the presence of one methoxy group in the molecule, and by converting the crystalline iodide thus obtained into the chloride a product was isolated identical with the delphinidin chloride obtained from violanin, oenidin, etc. For proof of its identity, its hydrate, crystalline form, colour of acid solution

Treatment before Test.	Petunidin Chloride.		Myrtillidin Chloride.	
	In 0·5 per cent. HCl.	In 3 per cent. HCl.	In 0·5 per cent. HCl.	In 3 per cent. HCl.
Deposited from MeOH — H_2O — HCl, then washed with EtOH .	Insoluble	Insoluble	Easily soluble	Insoluble
Same as above, after standing in air . .	As above		Easily soluble	Appreciably soluble
Crystallised from HCl .	Easily soluble	Insoluble	Easily soluble	Appreciably soluble
Crystallised from MeOH and HCl . . .	Easily soluble	Appreciably soluble	Easily soluble	Fairly easily soluble

in alcohol, solubility in dilute hydrochloric acid and in 7 per cent. sulphuric acid were examined.

Petunidin chloride differs from most of the monomethyl ethers of delphinidin that have been isolated, in that methoxy estimations show it to be homogeneous, no admixture of a dimethyl ether being present.

When petunidin chloride was carefully decomposed by hot caustic soda, one product consisted of pure *phloroglucinol*, containing no trace of a methoxy derivative, whilst a second contained 8·1 per cent. MeO, and was a derivative of *gallic acid*.

Petunin.

Petunin, a diglucoside of petunidin, has been isolated by Willstätter and Burdick from purple-blue petunia petals (*Petunia hybrida hort.*) ("Karlsruher Rathaus"), in which it occurs to the extent of about 15½ per cent. of their dry weight.

For the isolation of the colouring matter fresh petals were extracted with glacial acetic acid, the solution precipitated with ether, the product taken up in warm dilute (½—1 per cent.) hydrochloric acid, filtered, and allowed to stand, when the chloride separated in the form of long straight-cut prisms having a fine metallic lustre. The chloride was recrystallised from dilute hydrochloric acid.

Petunin chloride, $C_{28}H_{33}O_{17}Cl$, appears to form a crystalline hydrate of the composition $C_{28}H_{33}O_{17}Cl$, $2H_2O$, but as on drying the chloride loses hydrochloric acid as well as water, Willstätter and

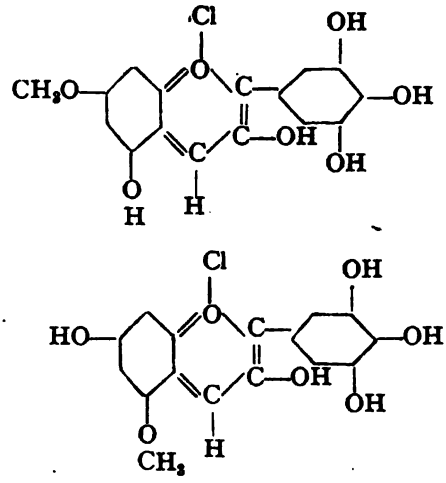
Burdick calculated their analytical figures to the chlorine-free base, when agreement was obtained with the formula $C_{28}H_{32}O_{17}$, and the loss of water and acid pointed to a hydrate of the above composition. The pure crystalline chloride consists of long rectangular tablets of a beautiful violet colour having a fine copper-coloured reflex. Air-dried, they sinter at 165° C. and melt at 178° C.

When a little water is added to the chloride, violet flakes, probably of a basic salt, are produced, but on addition of more water a clear red-coloured solution is produced, which, on acidification, turns red. Dilute aqueous solutions slowly become decolorised, rapidly if warmed, as the result of pseudo-base formation. The salt is difficultly soluble in cold dilute hydrochloric acid, more soluble if warm —at 20° C. 100 c.c. of 0·25 per cent. HCl dissolve 0·67 gr.; 0·5 per cent. HCl dissolve 0·45 gr.; 3 per cent. HCl dissolve 0·14 gr. of the crystalline hydrate, whilst at the same temperature 100 c.c. of 7 per cent. sulphuric acid dissolve 0·075 gr. Dilute sulphuric acid dissolves the chloride readily at first, the pigment being then reprecipitated as the crystalline sulphate; and hot 7 per cent. sulphuric acid dissolves considerable quantities of the chloride. In methyl alcohol the salt is very easily soluble, in ethyl alcohol, less so.

Ferric chloride, when added to a methyl alcoholic solution, gives a violet coloration, but if added to a solution in water, or ethyl alcohol, a blue (neither intense nor pure) colour results. Sodium carbonate produces a violet, then blue coloration when added to an acid solution, but if to a neutral solution containing some pseudo-base, a green-blue colour results, whereas if added to a solution of the pseudo-base, the colour obtained is yellow.

The distribution number of petunin chloride resembles that for normal diglucoside anthocyans, and on hydrolysis it yields *petunidin*—a monomethyl ether of delphinidin—(1 mol.) and *glucose* (2 mols.).

The Anthocyanidin isolated from the fruit of Vitis riparia, Michx. (*odoratissima*, J. Don).—Willstätter and Zollinger (Annalen, 1916, 412, 213) have isolated a glucoside anthocyan (at present unnamed) from the fruit of *Vitis riparia*, which has proved to be a monoglucoside of a monomethyl ether of delphinidin. There are reasons for assuming that it may be a new member of this series of methyl ethers, and should this be so, the structure of the chloride of the non-glucoside will be either—



or

There is, on the other hand, some reason to believe that this compound may prove identical with myrtillidin chloride, but the data available as the result of the interrupted work of these authors are still of a preliminary character.

As with most of the monomethyl ethers of delphinidin hitherto isolated, the figures obtained from it by means of Zeisel estimations are too high, and indicate the presence of some admixed dimethyl ether as impurity.

Vitis riparia anthocyanidin chloride crystallises in thin prisms which, when air-dried, contain 8·2 per cent. of water. It is easily soluble in 1 per cent. hydrochloric acid, but less so than ampelopsidin chloride; in 3 per cent. acid it is somewhat sparingly soluble; in 7 per cent. sulphuric acid it is easily soluble. On adding ferric chloride to an alcoholic solution, a pure blue colour is produced; if to an aqueous solution, blue-violet; the reaction is intense in both cases.

Vitis riparia anthocyanin—a monoglucoside of the above product—was isolated by Willstätter and Zollinger in a manner similar to that serviceable for ampelopsin, the skins only of the berries being used. The chloride which was obtained in a finely crystalline condition is easily soluble in methyl or ethyl alcoholic hydrochloric acid, and resembles ampelopsin chloride in its solubility in dilute acids.

Ferric chloride when added to an alcoholic solution produces a stable pure blue colour, whilst with an aqueous solution a violet colour results. Sodium carbonate produces a stable blue-violet or

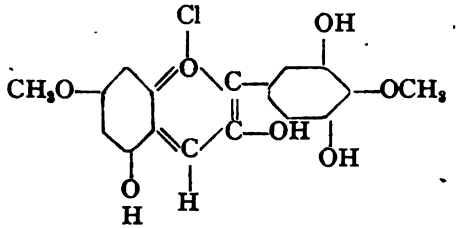
violet (according to concentration) when added to an acid solution, whereas caustic soda gives a fairly permanent blue with violet tinge. Hydrolysis of the pigment yields the above-described anthocyanidin chloride and glucose (1 mol.).

DELPHINIDIN DIMETHYL ETHERS AND THEIR DERIVATIVES.

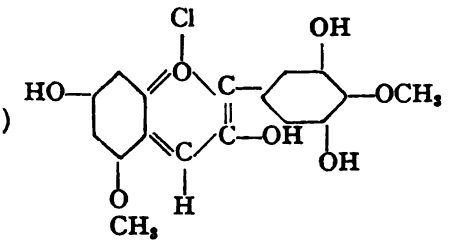
MALVIDIN.

Malvidin occurs as its diglucoside, *malvin*, in the flowers of the wild mallow, and has been examined by Willstätter and Mieg (Annalen, 1915, 408, 122), who have shown that it is a dimethyl ether of delphinidin, and have tentatively ascribed to its chloride the formula (1) or (2)—

(1)



(2)



The crystalline chloride is readily prepared by hydrolysis of the diglucoside—malvin chloride—by boiling for 2—3 minutes with 20 per cent. hydrochloric acid, in the manner usual for the preparation of anthocyanidins from their glucosides. The sugar-free compound separates almost completely after the hydrolysis.

Malvidin chloride, $C_{17}H_{15}O_7Cl$, as crystallised from 20 per cent. hydrochloric acid, has the form of long deep brown prisms, or needles, often in rosettes, which show a bronze reflex. These consist of the hydrate $C_{17}H_{15}O_7Cl$, $2H_2O$, which loses 1 molecule of water if dried in a vacuum desiccator at room temperature, the second only when dried in high vacuum at 105° C. Zeisel estimations show that this compound contains two methoxy groups. It does not melt below 300°.

The salt dissolves readily in cold alcohol, giving a fine violet-red-coloured solution which, on dilution with much water and heating, does not deposit the colour base but becomes colourless. In amyl alcohol the chloride is fairly easily soluble, yielding a violet-red solution which becomes violet when shaken with sodium acetate. With methyl alcohol it behaves somewhat peculiarly, in that the air-dried crystals dissolve, at first forming a purple-red solution, but very soon the pigment is deposited in the form of a crystalline precipitate that appears blue-red in reflex and violet by transmitted light (distinction from delphinidin and oenidin chlorides).

In dilute sulphuric acid the salt is difficultly soluble—this is its chief difference from oenidin chloride—whilst its sparing solubility in dilute hydrochloric acid differentiates it from delphinidin and oenidin. Even in 0·1 per cent. to 1 per cent. sulphuric acid the salt only dissolves temporarily, the red-brown solution rapidly depositing the sulphate as rosettes of needles, while the liquid becomes practically colourless, and with 7 per cent. acid similar changes occur (100 c.c. dissolve only 1·5 mg. of malvidin chloride at 15° C.). In 0·5 per cent. hydrochloric acid the salt is difficultly soluble cold, fairly soluble hot; in 1 per cent. acid it is almost insoluble cold and difficultly soluble hot, and in the concentrated acids it is practically insoluble.

When the chloride is rubbed with a little water, it is dissolved to an appreciable extent, the solution on warming becoming purple-red, whilst a dilute solution when boiled becomes decolorised owing to pseudo-base formation.

An acid solution when treated with caustic soda, or sodium carbonate, becomes first violet and then a fine blue colour, the latter being stable for hours if no excess of alkali is present. Ferric chloride gives no colour reaction, lead acetate produces a red-violet precipitate, Fehling's solution is reduced on boiling, and picric acid produces a crystalline precipitate of the difficultly soluble picrate which separates as small red-brown needles.

At the conclusion of the Zeisel estimations, fine brown crystals of the iodide of the demethylated pigment had separated, which, when converted to the chloride in the usual way (pptd. AgCl and MeOH . HCl) yielded a salt that was found to consist of *delphinidin chloride*. The identity of this was established by its crystalline form, the colour of its solutions, the difficult solubility in 7 per cent. sulphuric acid, easy solubility in 5 per cent. hydrochloric acid, and by the preparation of the pseudo-base.

The decomposition of malvidin chloride by fusion with caustic

potash was investigated by Willstätter and Mieg under the following conditions: 1 gr. of the salt was stirred into 50 gr. KOH in 16 gr. water, at 120° C., and the temperature then raised to 135—140° C. In a second operation the same procedure was adopted, but subsequently the temperature was taken to 170° C. for a time and then raised to 200° C., whereas in a third the final temperature was 250° C. It was ascertained that whereas the products from the latter experiment were *phloroglucinol* and *gallic acid*, in the second case *gallic acid monomethyl ether* was present (found MeO = 17·71 per cent.: theory requires MeO = 16·86 per cent.), whilst as a result of the first operation some *phloroglucinol monomethyl ether* could be detected (found MeO = 8·3 per cent.: theory requires MeO = 22·2 per cent.).

MALVIN.

Malvin—a diglucoside of malvidin—the colouring matter of the wild mallow (*Malva silvestris*, Linn.), occurs in the petals of that flower to the extent of about 6·4 per cent. of their dry weight. This pigment has been described by Willstätter and Mieg (*loc. cit.*).

Powdered, dry petals were used for the investigation, and these (3 kg. at a time) were extracted with 2 per cent. methyl alcoholic hydrochloric acid (10 litres), mixed with concentrated aqueous hydrochloric acid (300 c.c.), the extract filtered, and the residue washed once with the same solvent (4 litres). The extract (9½ litres) was precipitated by addition of ether (12 litres), vigorously agitating, as an almost solid dark mass from which the liquors were decanted. The purification consisted in dissolving the substance in cold methyl alcohol (1½ litres), filtering, and after adding absolute alcohol (1½ litres), reprecipitating by ether (6 litres), when the product (275 gr.) is pure enough for the next stage of the process, viz. the conversion of the chloride into the picrate. For the preparation of this latter the chloride was mixed (in 100 gr. portions) with an equal quantity of 1 per cent. hydrochloric acid, to prevent isomerisation, and a warm 1·5 per cent. solution of picric acid (1½ litres) added with constant stirring, the temperature being raised to 50° C., when the addition was complete. The pigment passed into solution, but on cooling and standing, glistening, hair-fine needles (50 gr. from 3 kg. of flower petals) separated. The picrate (25 gr.) was then dissolved in warm methyl alcohol (1 litre), and after cooling 70 c.c. of methyl alcoholic hydrochloric acid (containing 25 gr. HCl) added, the mixture filtered, and the chloride precipitated from the filtrate by addition of ether (3 litres). The product, after washing free from picric acid, by means

of ether, was recrystallised either from hot 1 per cent. hydrochloric acid, by adding more concentrated acid to its solution in cold 1 per cent. hydrochloric acid, or by slowly adding concentrated hydrochloric acid to a slightly warm solution of the pigment in 0·2 per cent. HCl, until 7 per cent. HCl was present.

Malvin chloride, $C_{29}H_{35}O_{17}Cl$, forms a hydrate of the composition $C_{29}H_{35}O_{17}Cl$, $8H_2O$, which crystallises in very long prisms or bundles of needles; in quantity these appear deep brown-red, and have a green reflex, but by transmitted light are purple-red. The salt has no melting-point, but begins to swell at 165° C. The crystalline hydrate loses all its water when dried in a vacuum desiccator at room temperature.

When air-dried it is rather difficultly soluble in water, giving bluish-red solutions, but these very rapidly become decolorised as the result of pseudo-base formation. In hydrochloric acid it is much more difficultly soluble than oenin chloride—in cold 1 per cent. acid very difficultly soluble, easily soluble in hot, whilst in cold 3 per cent. it is almost insoluble, but still fairly soluble hot. In 7 per cent. sulphuric acid it is appreciably soluble—0·03 gr. in 100 c.c.—the colour of the solutions being bluer than similar solutions of oenin chloride, or myrtillin chloride, but less blue than those of delphinin chloride; in concentrated sulphuric acid it is easily soluble with orange-red colour. In methyl alcohol the salt is easily soluble, rather less so in ethyl alcohol, the solutions having a fine purple-red colour; in hot amyl alcohol it is only appreciably soluble, and in most organic solvents it is insoluble.

With ferric chloride no colour reaction is produced; lead acetate produces a violet precipitate. Sodium carbonate gives a fine blue colour if added to a freshly prepared solution, but if to one that has stood a green, or yellow-green, owing to the presence of the pseudo-base which itself gives a yellow colour with this reagent. Sodium bisulphite produces a colourless easily soluble compound which is decomposed by acids; Fehling's solution is reduced by the salt when boiled.

Malvin chloride has a distribution number (1·6) of the same order as other normal diglucoside anthocyans, and on hydrolysis yields *malvidin chloride* (1 mol.) and *glucose* (2 mols.).

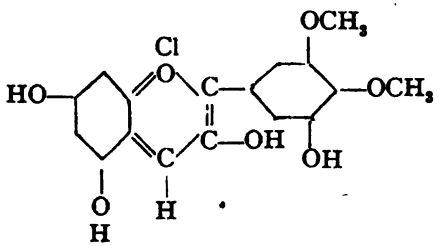
Malvin picrate (prepared as above) crystallises in brown-red to cherry-red needles which show a metallic reflex. It is fairly soluble in cold water, but difficultly soluble in a saturated solution of picric acid.

OENIDIN.

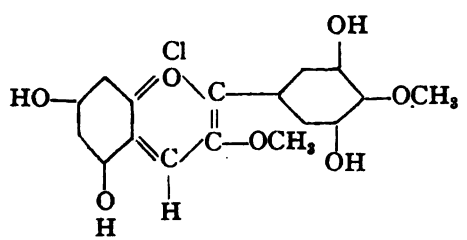
Oenidin, the product of the hydrolysis of oenin pigment of the black grape (or red wine), may be isolated when oenin chloride (1 gr. crystals) is dissolved in water (10 c.c.), 25 per cent. hydrochloric acid (50 c.c.) added, the whole rapidly heated to the boiling-point, boiled for three to four minutes, and then cooled and filtered. The oenidin chloride separates almost completely, even when the mixture is hot, and can be recrystallised from hot 3 per cent. hydrochloric acid. Willstätter and Zollinger (Annalen, 1915, 408, 83; 1916, 412, 195) were able to show that oenidin occurs, together with oenin, to the extent of a few per cent. of the total pigment, in black grapes (North Italian or hothouse), and in one exceptional case (hothouse) to the extent of 10 per cent. of the total.

Oenidin chloride, $C_{17}H_{15}O_7Cl$, forms a hydrate which crystallises in deep brown prisms or needles showing a dull bronze reflex, and has the composition $C_{17}H_{15}O_7Cl$, $1\frac{1}{2}H_2O$. When dried in high vacuum at 50° C. this hydrate gives the product $C_{17}H_{15}O_7Cl$, $\frac{1}{2}H_2O$, the last half molecule of water only being lost in high vacuum at 135° C.

Willstätter and Zollinger have tentatively ascribed to oenidin chloride either the structure—



or



The salt is readily soluble in water, and in a warm solution readily passes to the pseudo-base. Addition of hot water to an alcoholic solution does not precipitate the violet colour base (cf. cyanidin), whereas heating with acid reconverts the pseudo-base into colour salt. In methyl or ethyl alcohol the chloride is very readily

soluble, giving fine violet-red solutions; in cold 0·1 per cent. hydrochloric acid it is easily soluble, very easily if hot, in 1 per cent. it is still fairly soluble, in 3 per cent. difficultly soluble, more soluble hot, and may be crystallised from this, whilst 20 per cent. acid dissolves only 0·02 per cent. of the salt. In low concentrations of sulphuric acid (up to 7 per cent.) it is readily soluble.

Picric acid produces immediate precipitation of the very difficultly soluble picrate as fine deep red prisms. Sodium carbonate when added to an acid solution of the chloride gives a violet coloration, caustic soda a fine, but unstable blue, and lead acetate gives a blue-violet precipitate which on heating becomes blue. Ferric chloride gives no colour reaction but destroys the pigment (distinction from myrtillidin or althaein, and useful to detect the presence of these in red wines).

On demethylation by boiling with hydriodic acid and phenol (or acetic anhydride) Willstätter and Zollinger obtained *delphinidin iodide*. This by treatment with silver chloride and hydrochloric acid in alcoholic solution yielded the chloride, the identity of which was established by means of its solubility in 7 per cent. sulphuric acid and in 3 per cent. hydrochloric acid, also by its conversion into pseudo-base and sulphate.

Alkaline decomposition indicated that neither of the methoxy groups—Zeisel estimations showed that there are two in the molecule—is present in that portion of the molecule which yields phloroglucinol; whereas in the acidic product of decomposition the presence of a methoxy group was detected, a mixture of gallic acid and a methyl ether of an acid, probably methyl ether gallic acid itself, being isolated.

Oenin.

Oenin—a monoglucoside of oenidin—is the colouring matter of the black grape (North Italian or hothouse) and of red wine. It has received more attention than any other member of this series of colouring matters, but satisfactory chemical data concerning it only became available as the result of the work of Willstätter and Zollinger. In the grape skins this colouring matter appears to be accompanied by a small proportion of oenidin, and of a diglucoside (as yet unexamined) of this latter. Most of the early workers made use of red wine in their attempts to isolate the pigment, but on account of the small percentage present, the use of grape skins is much more convenient for this purpose.

In his book "Chemie des Weines" (Leipzig, 1856) Mulder described a method of isolating this pigment by precipitating the lead salt and decomposing this with sulphuretted hydrogen, but his product contained lead. The first attempt to use the lead salt for the isolation of an anthocyan pigment was described by Berzelius (Annalen, 1837, 21, 262).* The work of Mulder was followed by that of Glénard (Comptes rend., 1858, 47, 268; Ann. Chim. Phys., 1858, (3), 54, 366), who used ethereal hydrochloric acid for the decomposition of the lead salt, and he thus obtained an amorphous product to which he gave the name "oenolin," and assigned the formula $C_{20}H_{20}O_{10}$—the percentage composition of which does not differ greatly from that of $C_{22}H_{24}O_{12}$ now proved to be correct for the acid-free base. The method of Glénard was also employed by Gautier, who isolated a variety of compounds from related plants of the vine species, and was of the opinion that a whole series of these pigments occurred therein (Comptes rend., 1878, 86, 1507; 87, 64; 1892, 114, 623; 1911, 153, 531; cf. Willstätter and Zollinger, Annalen, 1916, 412, p. 198). Andree (Archiv f. Pharm., 1879, 13, 90) also attempted to isolate the pigment of the grape by the use of Mulder's method, whilst Heise (Arbeit. a. d. K. Gesundheitsamte, 1889, v., 618) described the preparation of two amorphous and impure products from red wine, using again the method of Glénard.

For the isolation of the pure pigment, as chloride or picrate, Willstätter and Zollinger (*loc. cit.*) extracted the pigment from the pressed skins of black grapes by means of glacial acetic acid (2—2½ times the weight of the skins). These were allowed to stand with the solvent in closed bottles for about a week, with occasional shaking, but even this treatment left some 10—20 per cent. of the pigment unextracted. After filtration the extract was precipitated with ether (3 vols.) when the pigment separated as a syrup containing all the colouring matter present in the extract, and from this the liquor was decanted, the residue being then washed with ether and dried by a current of air. The crude product thus obtained (from 8 kg. of skins) was dissolved in water (5 litres),† the

* Maumené gave the name "oenocyanin" to the product obtained by Mulder.

† It was found advantageous, in order to remove the small quantity of admixed oenidin, to dissolve the crude product in 0·5 per cent. HCl, instead of water, wash with amyl alcohol to remove oenidin, remove the alcohol by shaking with ether, and then add finely powdered picric acid to precipitate the picrate.

solution filtered, and an excess of cold aqueous picric acid (80 gr.) added which caused the separation of carmine-red flakes (17 gr.), but by heating the liquid and precipitate rapidly, and in small portions, and then allowing to cool, the picrate separated in bundles of carmine-red needles. Before conversion into the picrate, care had to be taken to remove all traces of acetic acid, and, to prevent the formation of the pseudo-base during the process, a little hydrochloric acid was added not only before the crude product was precipitated with ether, but also to the water used for its solution.

The picrate was reconverted into the chloride by dissolving (8·5 gr.) in methyl alcohol (200 c.c.), adding 17 per cent. hydrochloric acid (50 c.c.), and precipitating by the addition of ether (8 vols.), when the chloride separated as red-brown flakes, and was washed free from picric acid by ether (yield 6 gr.). The product, though amorphous, was practically pure and crystallised readily from a mixture of methyl and ethyl alcoholic HCl (MeOH 10 c.c., EtOH 25 c.c., 10 per cent. aqueous HCl 10 c.c.) if the alcohol was allowed to evaporate slowly (3 gr. amorphous yielded 1·7 gr. crystalline). In case the substance was required for analysis this operation was repeated several times.

As an alternative method of preparing oenin chloride, Willstätter and Zollinger made use of the fact that oenin, being a mono-glucoside anthocyan, is partially extracted from aqueous acid by amyl alcohol. They dissolved the crude product, obtained as for the previous preparation, in dilute hydrochloric acid, and extracted the solution with amyl alcohol, adding after each extraction acid to keep the volume of the aqueous layer constant. The first few amyl alcoholic extracts, which contained oenidin chloride, were neglected, the twenty further extracts made were agitated with about a quarter of their volume of 0·1 per cent. aqueous hydrochloric acid. The solution thus obtained, after washing free from amyl alcohol by means of ether, was treated with picric acid, whereby oenin picrate was obtained, and this was then reconverted into the chloride in the usual way. When crystallised from 7 per cent. hydrochloric acid oenin chloride separated in deep coloured prisms having a green reflex, and of the composition $C_{23}H_{25}O_{12}Cl$, $4H_2O$.

Oenin chloride, $C_{23}H_{25}O_{12}Cl$, forms a crystalline hydrate,

$$C_{23}H_{25}O_{12}Cl,\ 4H_2O\ .\ (?\ 6H_2O),$$

which usually consists of short deep-red prisms, singly or in clusters, showing a green reflex, though from some solutions it

separates as thin prisms. Its water is almost wholly lost when dried in a vacuum desiccator, and is completely removed in high vacuum at 50° C.

The salt is easily soluble in cold water, very easily in hot water, giving brown-red solutions, which on dilution become violet, and then colourless, but this decolorisation is prevented by the presence even of strong organic acids. Thus the colour of oenin chloride is stable, even in dilute solution, if the solution contains 0·2 per cent. of tartaric acid. In very dilute hydrochloric acid it is more soluble than delphinin or althaein chlorides, but less so than myrtillin chloride; in 2 per cent. it is very easily soluble, in 5 per cent. considerably so, in 10 per cent. but little soluble, and in 20 per cent. practically insoluble. In 7 to 10 per cent. sulphuric acid it is easily soluble; in methyl alcohol it is easily soluble, in ethyl alcohol less so, but much more soluble than myrtillin chloride. It is more soluble in a mixture of ethyl alcohol and water than in alcohol alone.

With sodium carbonate, an acid solution becomes blue to blue-violet, the colour being very stable on dilution; whereas caustic soda gives a violet-blue which on dilution becomes more violet, and is much more permanent than the colour given by myrtillin chloride. Lead acetate gives a fine deep blue precipitate, and copper sulphate a violet precipitate from aqueous solutions.

Owing to the fact that oenin chloride and malvin chloride give no colour reaction with ferric chloride in aqueous solution, whilst myrtillin chloride and althaein chloride give intense violet colorations, this reagent may be used to test red wine. If the colour of the wine is due to oenin, the grape pigment, very little change occurs on the addition of a drop of ferric chloride, but if the wine has been coloured by myrtillin (bilberry) or althaein (holly-hock), a deep violet colour is produced. The addition of malvin (field mallow) as a colouring matter to wine cannot be detected in this way as it also gives no reaction.

Oenin chloride is optically active, and like other anthocyans shows optical dispersion. The following observations have been recorded by Willstätter and Zollinger:—

Solutions in 0·1 per cent. HCl—

$$[\alpha]_{627} = -542^\circ\ (\pm 60^\circ),\ \text{i.e.}\ [M]_{627} = -2867^\circ.$$
$$[\alpha]_C = -421^\circ\ (\pm 30^\circ),\ \text{i.e.}\ [M]_C = -2227^\circ.$$

The absorption spectrum has been examined in dilute acid (7 per cent. H_2SO_4) and alcoholic solutions, and is described as

consisting of one broad band, whilst darkening also appears to occur in the violet. The data recorded are:—

Solution in 7 per cent. H_2SO_4, 1 mol. in 1760 litres.

Column	2·5 mm.	559 . 551 . . . 544 – 491 . 480
„	5·0 „	585 . 576 . . 563 – 406 . .

In ethyl alcohol, 1 mol. in 2500 litres.

Column	2·5 mm.	593 . . 588 – 518 . . 506
„	5·0 „	601 . . 597 – 494 . . 488/459 . .
„	10·0 „	605 . . 602 – 479 . .

This spectrum is very similar to that of myrtillin chloride.

Oenin chloride has a distribution number 10·4, hence in this respect it behaves as a normal monoglucoside. On hydrolysis it yields *oenidin chloride* (1 mol.) and *glucose* (1 mol.).

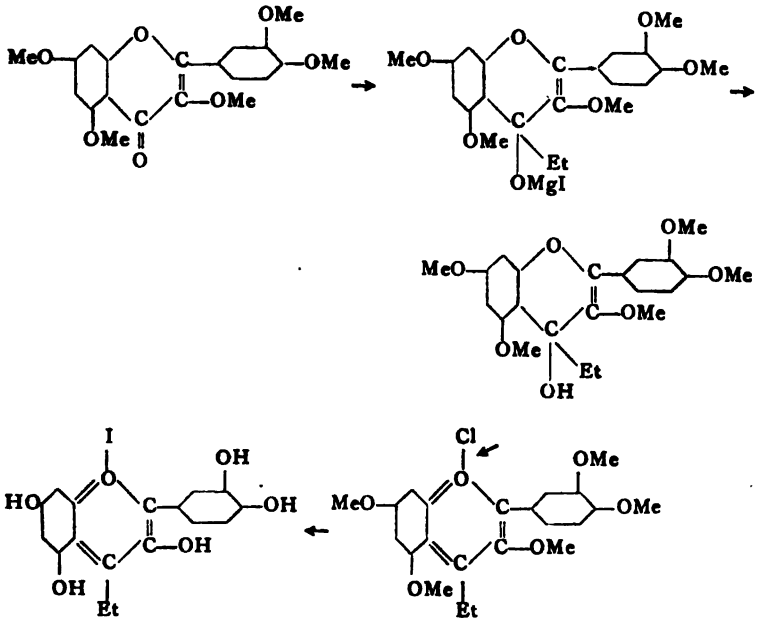
Oenin picrate is easily soluble in hot water, very difficultly soluble in cold water, easily in ethyl alcohol, and very easily so in methyl alcohol.

Note.—The colour reactions of anthocyan pigments with alum, described in several instances by Willstätter and his collaborators, appear to be due to the use by them of impure alum, and are really due to traces of iron salts present therein (Everest, Proc. Roy. Soc., 1918, B, 90, 251).

Synthetic Products of the Anthocyan Series.

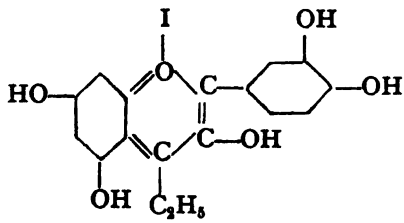
Mention has already been made of the synthesis of natural anthocyan pigments, but in addition to these, a number of interesting compounds of the same group have been prepared by Watson and his pupils (Chem. Soc. Trans., Watson and Sen, 1914, 397, and Watson, Sen, and Medhi, 1915, 1477) by treating natural colouring matters of the flavone, or flavonol series, after methylation, or ethylation, with various Grignard reagents, the products, on treatment with acid followed by demethylation, yielding substitution derivatives of the anthocyan series.

Employing quercetin penta-methyl ether the series of changes may be represented thus:—



In this way the following products have been obtained :—

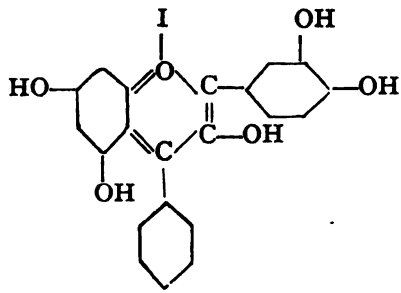
3 : 5 : 7-*trihydroxy*-2-*m* : *p*-*dihydroxyphenyl*-4-*ethyl*-1 : 4-*benzo-pyranol-anhydriodide*, crimson needles, which dissolve in alkalis with a blue colour—



The *colour base*, prepared by the action of sodium acetate on the iodide, is described as a dark violet solid, the *penta-ethyl ether* (iodide) as crimson needles (from alcohol), melting-point 169° C., and the *tri-ethyl ether*, prepared by the partial de-ethylation of penta-ethyl ether by means of aluminium chloride, as an almost black powder.

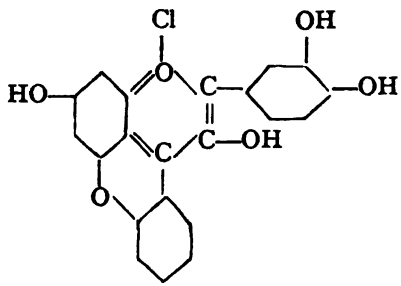
The *tri-methyl ether*, from quercetin tri-methyl ether, crystallises in red needles, melting-point 163—165° C.

3 : 5 : 7-*trihydroxy-2-m* : *p-dihydroxyphenyl-4-phenyl-1* : 4-*benzopyranol-anhydriodide*, forms dark red prismatic crystals—

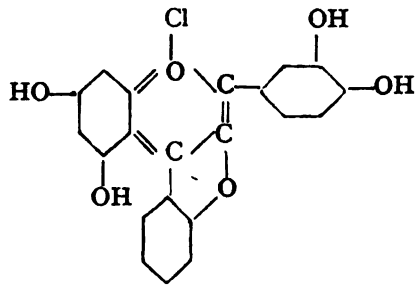


and its *tetra-ethyl ether*, bright red needles.

The *internal anhydride* from 3 : 5 : 7-*trihydroxy-2-m* : *p-dihydroxyphenyl-4-o-hydroxyphenyl-1* : 4-*benzopyranol-anhydrochloride*, dark red needle-shaped crystals with blue reflex, has one of the following formulæ—

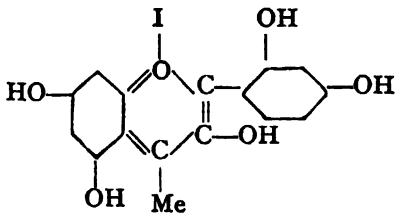


or

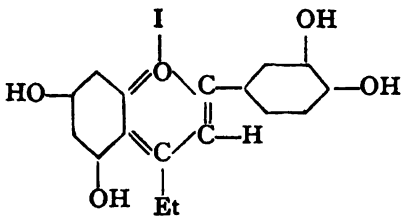


From the corresponding *hexa-ethyl ether*, crimson crystals, a ferrichloride, melting-point 190° C., was obtained.

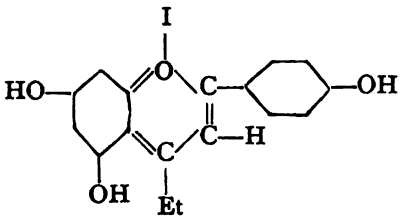
3 : 5 : 7-*trihydroxy-2-o. p. dihydroxyphenyl-4-methyl-1* : 4-*benzopyranolanhydroiodide* (crystalline form not stated), dissolves in alkalis with a crimson colour—



5 : 7-*dihydroxy*-2-*m* : *p*-*dihydroxyphenyl*-4-*ethyl*-1 : 4-*benzopyranol-anhydroiodide*, *tetra-ethyl ether*, crystallises in orange needles, melting-point 169—172° C.—

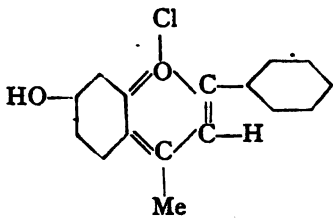


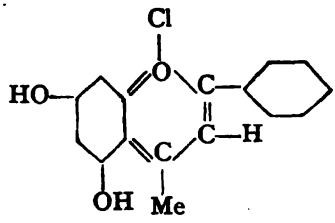
5 : 7-*dihydroxy*-2-*p*-*hydroxyphenyl*-4-*ethyl*-1 : 4-*benzopyranol-anhydroiodide*, needle-shaped crystals, dissolves in alkalis with crimson colour—

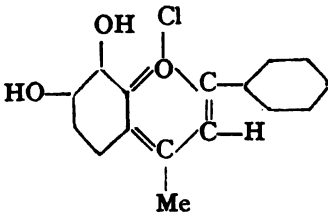


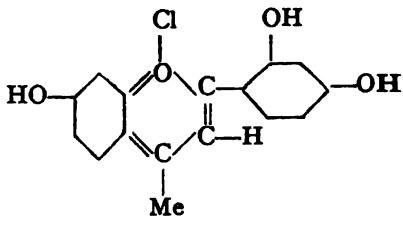
The *tri-ethyl ether*, orange coloured rhombic crystals, melts at 178—180° C.

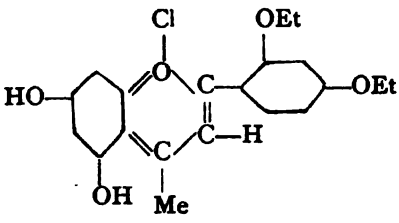
A considerable number of compounds of this type related to flavones have been synthesised by Bülow (Ber., 1901, 34, 1189, and 1782; 1903, 36, 1941, 2292, and 3607; 1904, 37, 354, and 4715; 1906, 39, 214, and 2027) from resorcinol, phloroglucinol, or pyrogallol, by condensation with derivatives of acetylacetone, benzoylacetone, or benzoyl acetophenone, usually in glacial acetic acid, in the presence of hydrochloric acid. In this way the following have been prepared :—

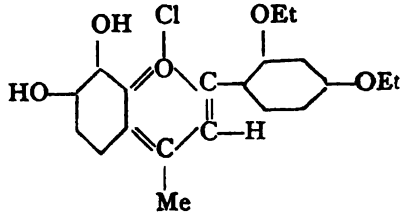

Cl
HO
O
C
C—H
C
Me

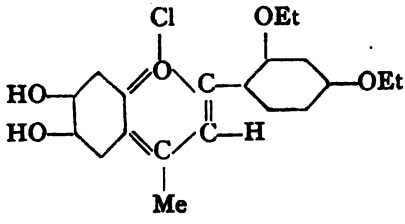

Cl
HO
O
C
C—H
C
OH
Me

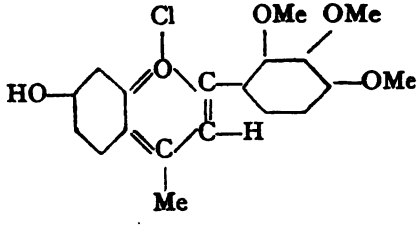

OH
Cl
HO
O
C
C—H
C
Me

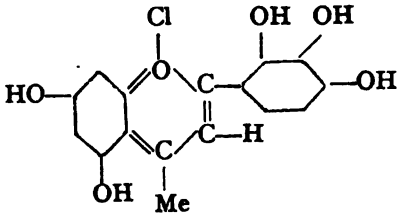

Cl
OH
HO
O
C
OH
C—H
C
Me

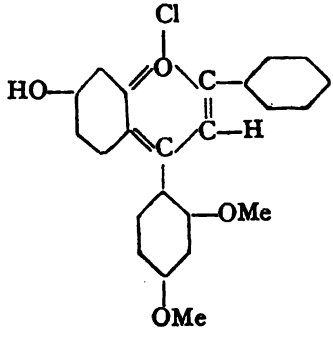

Cl
OEt
HO
O
C
OEt
C—H
C
OH
Me

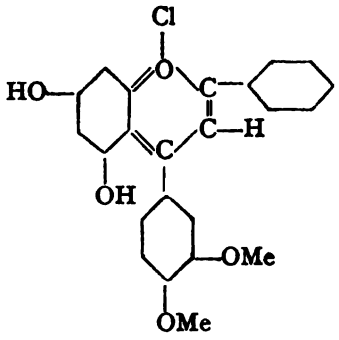

OH
Cl
OEt
HO
O
C
OEt
C—H
C
Me

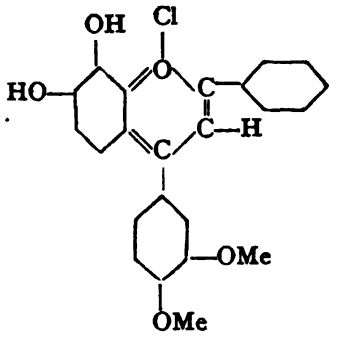

Cl
OEt
HO
HO
O
C
OEt
C—H
C
Me


Cl
OMe
OMe
HO
O
C
OMe
C—H
C
Me

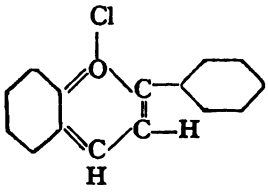

Cl
OH
OH
HO
O
C
OH
C—H
C
OH
Me

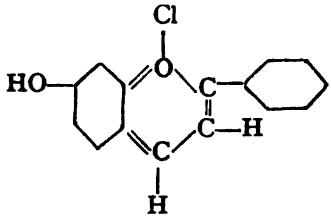

Cl
HO
O
C
C—H
C
OMe
OMe

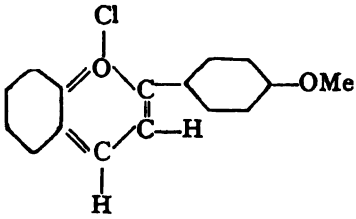


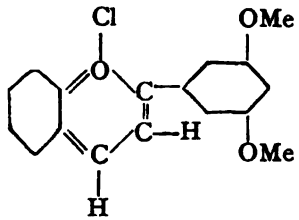


Finally, simple members of this series—also related to flavones—have been prepared by Decker and Fellenberg (Ber., 1907, 40, 3815) and W. H. Perkin and Robinson (Chem. Soc. Trans., 1908, 1085) from hydroxy-aldehydes (e.g. resorcyl aldehyde) and ketones (e.g. acetophenone), or by the action of Grignard reagents on coumarin. In this way the mother substance of the series—*2-phenol-1 : 4-benzopyranol-anhydrochloride* — was obtained, as also the hydroxy and methoxy compounds represented by the following formulæ :—









Carajura and Chica Red.

These are rare pigments prepared by the Indians of Central America from species of *Bignonia* which are very similar in appearance and may contain as a basis the same colouring matter. A red pigment of this character, evidently "Chica red," is referred to in

"The Travels and Researches of Baron Humbolt" (Macgilivray, Edinburgh, 1836, p. 229): "Red paint is the ordinary decoration of these tribes. The most common kind is obtained from the seeds of the *Bixa orellana* and is called annotto, achoute, or roucou. Another more expensive species is extracted from the leaves of the *Bignonia chica.*" According to Crookes ("Dyeing and Calico Printing," 1874, 388) chica is obtained from the leaves of the *B. chica* which the Indians boil with water, and add some particles of the bark known as "aryane" to the decanted liquid which causes the precipitation of the colouring matter.

An interesting résumé of what is known of this subject is given by Holmes (Pharm. J., 1901), who states that preparations very similar to carajura are employed by the South American Indians in Brazil, Bolivia, and Guiana. These include chica from the leaves of *B. chica*, from "ula" leaves derived from an unknown species of *Bignonia* in Bolivia, and a pigment prepared from the heartwood of the *B. tecoma* in Minas (Brazil). The latter, according to Lee (Chem. Soc. Trans., 1901, 284), is prepared by mixing the dust and shavings of this tree with slaked lime and heating the mass with water. From the *B. tecoma* Lee isolated a considerable amount of a yellow crystalline compound, *tecomin*, which is referred to later.

Carajura or Crajura was apparently first examined by Virey (Journ. de Pharmacie et Chimie, (3), 5, 154). The sample experimented with, which came from Para, was soluble in alkalis and was precipitated therefrom by acid, and is stated to have been prepared by the Galibis by boiling with water the stem and leaves of an unknown species of *Bignonia* when the latter in the autumn had acquired a purple colour.

Crookes states (*loc. cit.*) that chica is soluble in 36 per cent. alcohol, in ether and in alkalis with a vinous red colour, and when heated in a sealed tube with alkali and glucose gives a bluish-red liquid which becomes brown on exposure to air and then yields on acidification an orange-red precipitate.

As the result of an examination of chica red or carajura said to be derived from the leaves of the *Bignonia chica*, Erdmann (Jahres., 1857, 487) assigned to the colouring matter which he isolated by extraction with alcohol the formula $C_8H_8O_3$. This substance was soluble in caustic alkali but not in alkali carbonate solutions, and when oxidised with chromic acid gave *anisic acid*, whereas with nitric acid picric acid was produced.

Perkin (Proc. Chem. Soc., 1914, 30, 212), who examined a sample

of "carajura" obtained from Messrs. Wright, Layman, and Umney of London, and which is referred to in the paper of Holmes (*loc. cit.*), found this to contain a small quantity of the calcium lake of two colouring matters which had either been precipitated on, or intermingled with a substance of the nature of ground bark or peat. After treatment with hot dilute hydrochloric acid, alcohol removes the colouring matters in the form of a resin, and from this, by means of boiling benzene, *carajurin* is isolated. This compound to which the formula $C_{18}H_{16}O_5$ has been provisionally assigned separates in ruby needles, melting at 204—206°, is soluble in boiling dilute alkali with a red colour, and is nearly devoid of dyeing properties. With mineral acids it very readily yields oxonium salts, crystallising in bright, orange needles, of which the *sulphate*, probably $C_{18}H_{16}O_5 . H_2SO_4 . H_2O$ is the most stable, the *hydrobromide* and *hydrochloride* being decomposed at 100°. From the hydrochloride a *platinichloride* can be prepared. Cold acetic anhydride with a trace of pyridine, after two days, gives an almost colourless *acetyl* compound, crystallising in needles, whereas bromine gives an immediate precipitate with carajurin in acetic acid, which when boiled with this solvent, separates in orange needles. Hydriodic acid converts carajurin with loss of 2 molecules of methyl iodide and probably also of a molecule of water into a substance provisionally termed *carajuretin iodide*, bright scarlet needles, stable in the presence of cold water, and from this by means of cold pyridine, *carajuretin*, $C_{16}H_{12}O_5$, scarlet needles, melting above 330°, and soluble in alkalis with a reddish-violet colour, is produced. By dry distillation carajurin evolves a trace of aromatic oil, resembling anisaldehyde in odour, and when fused with alkali, *p-hydroxybenzoic acid* and a colourless *substance*, melting at 185—187°, as yet unidentified, are obtained. In many respects carajurin resembles the anhydrohydroxybenzopyranol compounds described by Bülow and Wagner (Ber., 1901, 34, 1199).

That portion of the alcoholic extract insoluble in benzene yields to ether *carajurone*, isolated as a scarlet powder, which readily assumes a beetle-green lustre, and possesses strong dyeing properties. Analysis indicates the presence of more oxygen in this compound than in carajurin. A small amount of a similar, but brighter lake from British Guiana, and obtained from the leaves of a "bushrope," gave a colouring matter dyeing alizarin-like shades. This preparation, considered to be "chica red," appeared to differ in some respects from the "carajura" above described.

BIGNONIA TECOMA.* TECOMIN.

The *Bignonia tecoma* is a somewhat common tree in the uplands of Minas, Brazil, which when fully grown is about 30 feet high and in September is covered with brilliant yellow flowers. The natives mix the sawdust and shavings of this tree with slaked lime, heat the mass with water and employ the resulting bath to dye cotton cloth. A paste made of the sawdust mixed with lime is also used to stain lighter coloured woods a deep brown. By exhausting the sawdust with boiling 85 per cent. alcohol and concentrating the extract, Lee (Chem. Soc. Trans., 1901, 79, 284) isolated the colouring matter *tecomin*, which has been previously referred to. This, which has apparently not been submitted to analysis, forms shining chrome yellow crystals possessing a nacreous lustre, soluble in alkalis with a rose-red coloration.

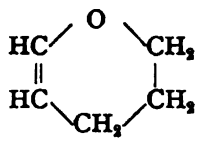
A further quantity of this compound could be isolated from the alcoholic filtrate, the total amount thus given by the wood being approximately 5 per cent.

The sawdust extracted with alcohol contains a deep brown dye which may now be removed from it by alkalis, and by acidification this is deposited therefrom as an amorphous brown powder. Nothing is at present known as regards the relationship, if such exists, between tecomin and the colouring matter of chica red or carajura.

* According to Holmes (*loc. cit.*) the name *Bignonia tecoma* does not appear in the Kew Index, but only *Bignonia tecomoides*, which is, however, a shrubby species.

CHAPTER IX.

DIHYDRO-PYRAN GROUP.



Brazilwood—Logwood—African Logwood or *Hæmatoxylon africanum*.

BRAZILWOOD.

UNDER the name of Brazilwood certain varieties of the so-called "soluble" red woods are known, the term "soluble" being employed to distinguish them from the dyestuffs of the barwood class, which only with difficulty yield their colouring matters to boiling water. These soluble red woods give with aluminium mordanted fabrics a bright-red shade, which in each case is derived from one and the same colouring matter, and all are botanically allied, in that they consist of the wood of various species of *Caesalpinia*. About nine varieties have been employed as dyestuffs, of which the following are the best known.

Fernambuco or Pernambuco wood is considered to be the richest in colouring matter, and is the product of the *Caesalpinia crista*, a tree which is abundant in Jamaica and Brazil.

The true Brazilwood is derived from the *Caesalpinia braziliensis*, and is said to contain only one-half the colouring matter which is present in the Fernambuco variety. It is obtained exclusively from Brazil.

Sappanwood is obtained from the *Caesalpinia sappan*, a tree which is common to the warmer regions of Asia. The so-called Limawood is a variety of sappan, and the dyewood imported from the Philippine Islands is an inferior quality of this product.

Peachwood is the product of the *Caesalpinia echinata*, which occurs in Central America and the northern parts of South America.

These woods, which are very hard, and of a deep red colour, come into the market in the form of billets varying in weight from a

few pounds up to a hundredweight. If freshly cut the internal colour of the wood is seen to be light yellow, but this soon changes to deep red in contact with air.

Some varieties of these woods were employed for dyeing purposes in India long before the discovery of America, and it is stated that when South America was discovered by the Spaniards, in 1500, the northerly portion of the country was named Brazil (from *brasa*, fiery red), because this red dyewood was found there in such immense quantities.

Owing to the fugitive character of the colours yielded by Brazilwood it is now only employed to a somewhat limited extent.

Brazilin, $C_{16}H_{14}O_5$, the colouring principle of Brazilwood, was first isolated in a crystalline condition by Chevreul (Ann. Chim. Phys., (1), 66, 225); but was not further examined until 1864, when Bolley (Schweiz. poly. Zeitsch., ix., 267) assigned to it the formula $C_{22}H_{20}O_7$. Subsequently Kopp (Ber., 6, 446) proposed the formula $C_{21}H_{18}O_7$, but it was left to Liebermann and Burg (Ber., 9, 1883) to determine the exact composition of this substance, and their formula, $C_{16}H_{14}O_5$, is in use at the present time. To prepare brazilin from the wood itself, it is best to employ the commercial extract. This is stirred up with a considerable quantity of sand, the product extracted with cold ether, the ethereal liquid evaporated to a small bulk, treated with a little water, and allowed to stand for some days. Crystals slowly separate, and these are purified by crystallisation from a little water.

This method is, however, tedious, and the usual source of brazilin consists of the crude crystalline crusts of this substance which are frequently deposited from Brazilwood liquor, an intermediate product in the manufacture of Brazilwood extract. The crude substance is best purified by two or three crystallisations from water, to which a little sulphurous acid has been added (Gilbody and W. H. Perkin, and Yates, Chem. Soc. Trans., 1901, 79, 1396). Brazilin crystallises in two forms, either as colourless needles containing $1\frac{1}{2}H_2O$, or as colourless prisms with $1H_2O$. It is readily soluble in alcohol and water, and dissolves in a dilute solution of sodium carbonate with a beautiful carmine-red colour.

Tetraacetylbrazilin, $C_{16}H_{10}O_5(C_2H_3O)_4$, colourless needles, melting-point 149—151° (Liebermann and Burg); *triacetylbrazilin*, $C_{16}H_{11}O_5(C_2H_3O)_3$, needles, melting-point 105—106° (Buchka and Erck, Ber., 18, 1139); *brombrazilin*, $C_{16}H_{13}BrO_5$, brown-red leaflets (Buchka and Erck); *dibrombrazilin*, $C_{16}H_{12}Br_2O_5$, leaflets (Schall and Dralle, Ber., 23, 1550); *tetraacetylbrombrazilin*, $C_{16}H_9BrO_5(C_2H_3O)_4$,

needles, melting-point 203—204° (Buchka, Annalen, 17, 685); *tetraacetyldibrombrazilin*, $C_{16}H_8Br_2O_5(C_2H_3O)_4$, melting-point 185° (Schall and Dralle); *tribrombrazilin*, $C_{16}H_{11}Br_3O_5$ (Schall and Dralle); *dichlorbrazilin*, $C_{16}H_{12}Cl_2O_5$ (Liebermann and Burg); and *tetrabrombrazilin*, $C_{16}H_{10}Br_4O_5$, fine red needles (Buchka and Erck), have been prepared.

When brazilin is methylated with methyl iodide in the usual manner, it gives *brazilin trimethyl ether* (Schall and Dralle, Ber., 20, 3365; Herzig, Monatsh., 14, 56; and Schall, Ber., 27, 525), $C_{16}H_{11}O_5(OCH_3)_3$, prisms, melting-point 138—139°, which on acetylation yields *acetylbrazilin trimethyl ether*, $C_{16}H_{10}O_5(OCH_3)_3(C_2H_3O)$, melting-point 171—173° (Herzig, Monatsh., 15, 140; Schall, Ber., 27, 326).

According to Gilbody, W. H. Perkin and Yates (Chem. Soc. Trans., 79, 1403), large quantities of the trimethyl ether are conveniently prepared as follows: 143 grams of brazilin dissolved in the smallest possible quantity of methyl alcohol are treated with 35 grams of sodium in methyl alcohol and methyl iodide (250 grams) and the mixture is heated fifty hours to 60—65° in absence of air. A second method, employed also by v. Kostanecki and Lampe (Ber., 35, 1669), consists in methylating brazilin with excess of dimethyl sulphate and alkali.

The difficulty experienced in fully methylating brazilin is evidence of the presence of an alcoholic group; but the *tetramethyl ether*, $C_{16}H_{10}O(OCH_3)_4$, melting-point 137—139°, has been prepared by Schall by treating the sodium compound of the trimethyl derivative suspended in benzene with methyl iodide at 120° (compare also Herzig, *loc. cit.*). From this substance the following derivatives have been prepared:—

Brombrazilin tetramethyl ether, $C_{16}H_9BrO.(OCH_3)_4$, prisms, melting-point 180—181° (Schall and Dralle, Ber., 21, 3014), and *dibrombrazilin tetramethyl ether*, $C_{16}H_8Br_2O.(OCH_3)_4$, melting-point 215° (Schall and Dralle, Ber., 23, 1432).

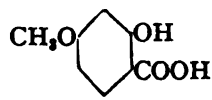
When brazilin is submitted to dry distillation, it gives *resorcin* (Kopp, *loc. cit.*), and by fusing it with potassium hydroxide Liebermann and Burg obtained resorcin, and Herzig (Monatsh., 27, 739) *protocatechuic acid*. With nitric acid brazilin yields trinitroresorcinol (Reim, Ber., 4, 334).

When brazilin, the colouring principle, is oxidised under suitable conditions, it is converted into *brazilein*, the true colouring matter, $C_{16}H_{14}O_5 + O = C_{16}H_{12}O_5 + H_2O$, and for this purpose the action of air on an alkaline brazilin solution, alcoholic iodine (Liebermann

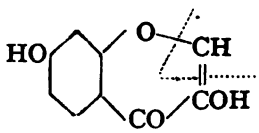
and Burg), potassium nitrite and acetic acid (Schall and Dralle), nitric acid in the presence of ether (Buchka and Erck), and sodium iodate (Mayer, Zentr., 1904, i., 228) have been employed. It can, however, be more economically prepared from Brazilwood extract in the following manner (Hummel and A. G. Perkin, Chem. Soc. Trans., 1882, 41, 367):—

To an aqueous solution of the extract of the wood an excess of ammonia is added, and air is aspirated through the liquid. A precipitate of the impure ammonium salt of brazilein gradually separates, and this is collected, dissolved in hot water, and treated with dilute acetic acid (sp. gr. 1·04). A brown viscous precipitate of the crude colouring matter is thus obtained, which is extracted with hot dilute acetic acid, and the extract evaporated on the water-bath. Crystals of brazilein separate, which are collected and washed with acetic acid.

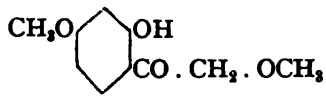
Brazilein consists of minute plates possessing a strong metallic lustre, and by transmitted light a reddish-brown colour. It is very sparingly soluble in all the usual solvents, and cannot be recrystallised in the ordinary manner. It is in reality the colouring matter of Brazilwood, and possesses strong tinctorial property. Alkaline solutions dissolve it with a deep-red coloration, which on standing in air passes gradually to brown. A study of this oxidation was carried out by Schall and Dralle, with interesting results. 2·7 grams of brazilin dissolved in 150 c.c. of water was treated with 10 c.c. of sodium hydroxide solution (sp. gr. 1·37), and air aspirated through the liquid for thirty-six hours. Ether extracted from the acidified solution *β-resorcylic acid*, and a substance $C_9H_8O_4$, crystallising in brownish-yellow needles, melting-point 271°, gave a *diacetyl* compound, melting-point 148—149°, and a *dimethyl* ether, melting-point 169—170°. When the latter was oxidised in acetic acid solution, with potassium permanganate *β-resorcylic acid monomethyl ether* was produced:—



Schall and Dralle considered that this compound was probably a pheno-γ-pyrone derivative, and Feuerstein and v. Kostanecki (Ber., 32, 1024) proved that this was in reality the case, and assigned to it the following constitution:—



Thus the dimethyl ether, when hydrolysed with alcoholic potash, gave *fisetol dimethyl ether*—

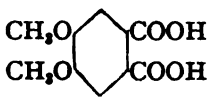


a substance which had already been obtained in a similar manner by Herzig from fisetin tetramethyl ether (see Young Fustic).

Our chief knowledge of the constitution of brazilin is due to the elaborate investigations of W. H. Perkin and his pupils, who obtained most important results by the oxidation of brazilin trimethyl ether with potassium permanganate, and also with chromic acid.

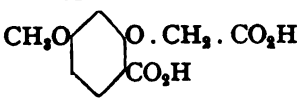
Gilbody, Perkin, and Yates (Chem. Soc. Trans., 1901, 79, 1465) found that when brazilin trimethyl ether is oxidised with permanganate, it gives, in addition to oxalic, acetic, and formic acids, the following compounds:—

1. *m-Hemipinic acid*—

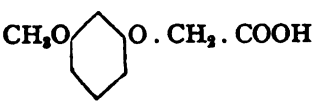


The isolation of this substance was important, since it showed that brazilin contains a catechol nucleus and two orthohydroxyls, and as a result of these latter no doubt in part its tinctorial properties are due.

2. *2-Carboxy-5-methoxyphenoxyacetic acid*—

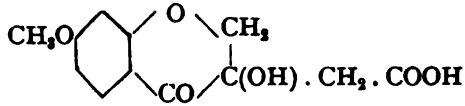


On fusion with alkali this compound yields resorcinol, and on heating with water to 200° is converted into *methoxyphenoxyacetic acid*—

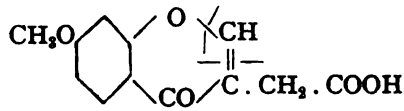


This can be synthesised by the interaction of ethylbromacetate with the sodium compound of resorcinol monomethyl ether and subsequent hydrolysis.

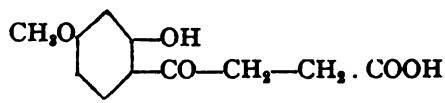
3. *Brazilic acid*—



when fused with alkali gives resorcin, and on warming with sulphuric acid is converted into *anhydrobrazilic acid*—

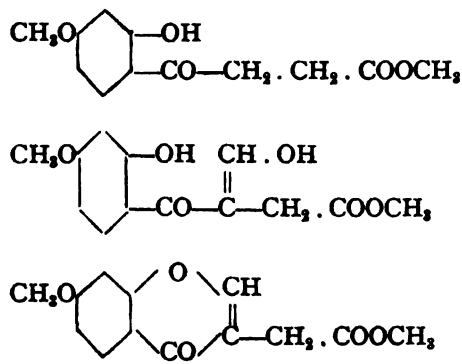


Boiling baryta water hydrolyses anhydrobrazilic acid, with production of *formic acid* and 6-*hydroxy*-4-*methoxybenzoylpropionic acid*—

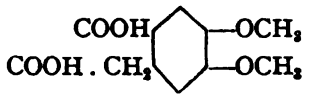


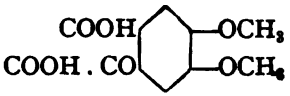
On methylation this is converted into the dimethyl ether, and the latter can be produced by the interaction of dimethylresorcinol and the half chloride of succinic acid monoethyl ester, and subsequent hydrolysis. It is also formed when resorcinol dimethyl ether and succinic acid are treated with aluminium chloride without employing a solvent.

Finally, when the methyl ester of this hydroxymethoxybenzoylpropionic acid is dissolved in ethyl formate and treated with sodium, the *methyl ester* of *anhydrobrazilic acid* is produced. This interesting synthesis may be represented as follows:—

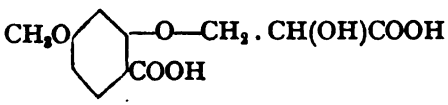


Dimethoxycarboxybenzylformic acid (1), and *dimethoxycarboxybenzoylformic acid* (2)—

(1) 

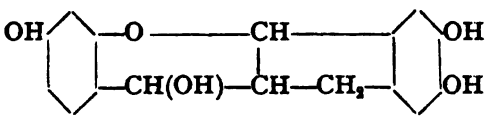
(2) 

represent intermediate stages in the formation of *m*-hemipinic acid from brazilin trimethyl ether, whereas the acid



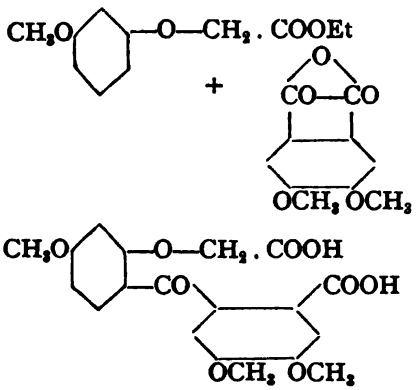
also isolated, is, no doubt, that product of the oxidation which is anterior to the formation of carboxymethoxyphenoxyacetic acid (see above).

The earlier work suggested the following probable constitution for brazilin :—



but this, as a result of the investigation of brazilinic acid, a very important substance, also produced by the oxidation of brazilin trimethyl ether, was subsequently discarded.

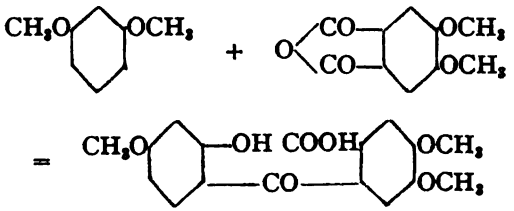
Brazilinic acid.—The constitution of this acid has been conclusively demonstrated by its synthesis, which has been effected by the interaction of *m*-hemipinic anhydride with ethyl methoxyphenoxyacetate in the presence of aluminium chloride. This is illustrated by the following equation :—



Brazilinic acid.

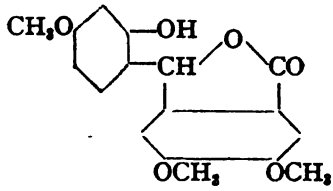
When brazilinic acid is reduced with sodium amalgam, it is quantitatively converted into *dihydrobrazilinic acid*, $C_{19}H_{20}O_9$, which at once loses water with the formation of the *lactone*, $C_{19}H_{18}O_8$.

To synthesise the latter compound, *m*-hemipinic anhydride is condensed with resorcinol dimethyl ether to form *2-hydroxy-4 . 5′ . 4′-trimethoxybenzoylbenzoic acid*—

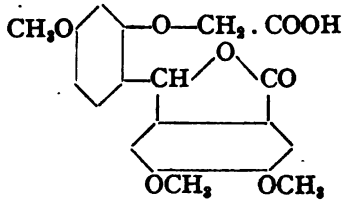


When reduced with sodium amalgam, this acid gives *2-m-meconyl-5-methoxyphenol* (1), and this by the action of chloracetic acid and potassium hydroxide is converted into the lactone of dihydrobrazilinic acid (2)—

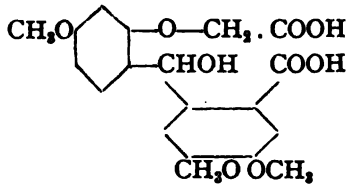
(1)



(2)

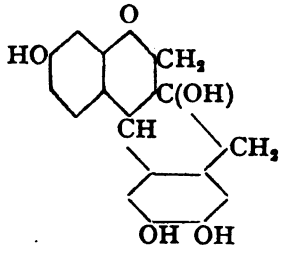


(3)



Dihydrobrazilinic acid itself is accordingly represented by formula (3).

The following constitution—



has, as a result of this work, been assigned to brazilin by Perkin and Robinson (Chem. Soc. Trans., 1908, 93, 496), and is in complete harmony with the facts above enumerated.

Oxidation of trimethylbrazilin with chromic acid.

When trimethylbrazilin is oxidised with chromic acid it is converted into *trimethylbrazilone* (Gilbody and Perkin, *v. infra*)—

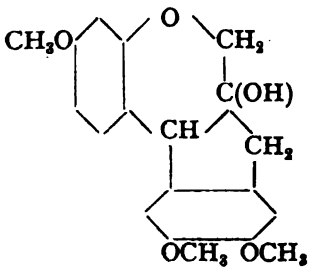
$$(CH_3O)_3C_{16}H_{11}O_2 + 2O = (CH_3O)_3 . C_{16}H_9O_2 + H_2O,$$

and this apparently simple reaction has proved to be of an extremely puzzling character.

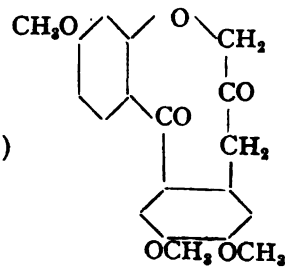
When trimethylbrazilone is oxidised with permanganate, it gives *m-hemipinic acid*, *2-carboxy-5-methoxyphenoxyacetic acid*, *brazilic acid*, *dimethoxycarboxybenzoylformic acid*, *dimethoxycarboxybenzylformic acid*, *methoxycarboxyphenoxylactic acid*, and *brazilinic acid*.

In an earlier paper, Gilbody and Perkin (Chem. Soc. Trans., 1902, 81, 1040) suggested for trimethylbrazilone a constitution based upon their first formula for brazilin (see above), but it has now been shown (*ibid.*, 1908, 93, 498) that the reaction proceeds in the following manner: By the oxidation of trimethylbrazilin (1) with chromic acid a disruption of the central linkage occurs, with the formation of an unstable diketone (2), and this subsequently undergoes aldol condensation, and trimethylbrazilone is produced (3)—

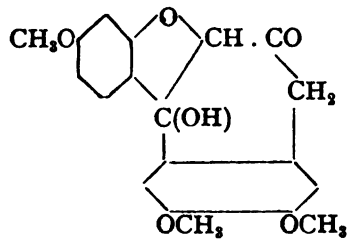
(1)



(2)

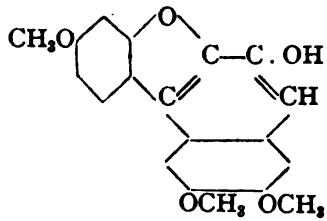


(3)



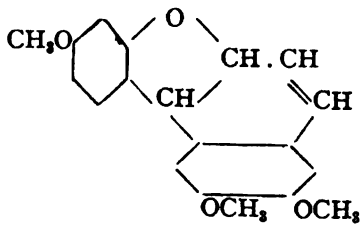
This formula represents trimethylbrazilone as a derivative both of coumaran and tetrahydronaphthalene, and affords a ready explanation of the decomposition products of this compound.

An important point in favour of this constitution is afforded by the behaviour of trimethylbrazilone with alkalis, or acetic anhydride and other dehydrating agents, for it is thus converted with loss of 1 molecule of water into *anhydrotrimethylbrazilone*, $(CH_3O)_3C_{16}H_7O_2$. There can be little doubt that the formation of this substance is due to the elimination of water from the aldol grouping in trimethylbrazilone, and that it possesses the following formula :—



Anhydrotrimethylbrazilone is thus a derivative of *β-naphthol*, and it possesses many of the properties of this substance. It is soluble in dilute alkali, and this solution gives with diazobenzene chloride a red azo-dyestuff. Diazonaphthalene chloride behaves similarly, and the dye thus produced dissolves in sulphuric acid with a blue colour.

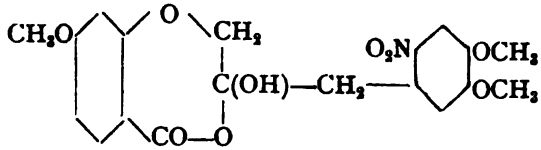
When trimethylbrazilone is boiled in acetic acid solution with phenylhydrazine, *deoxytrimethylbrazilone*, $C_{16}H_9O_3(CH_3O)_3$, is obtained, and this is probably a dihydronaphthalene derivative of the formula—



The most striking reaction of trimethylbrazilone is its behaviour with nitric acid, when it yields a compound possessing the composition of a nitrohydroxydihydrotrimethylbrazilone—

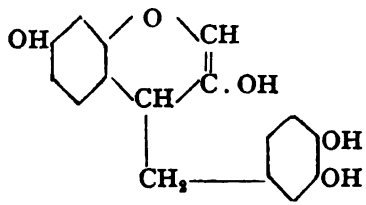
$$C_{16}H_9O_3(CH_3O)_3 + HNO_3 = C_{16}H_{10}O_6N(CH_3O)_3.$$

This substance dissolves in alkali with a purple colour, but on standing the colour rapidly fades, *o*-nitrohomoveratrol separates, and the solution contains *p*-methoxysalicylic acid. Oxidation with permanganate gives 2-carboxy-5-methoxyphenoxyacetic acid, and these decompositions point clearly to the formula—



as representing the constitution of this nitro compound (see also Perkin and Robinson, *ibid.*, 1909, 95, 381).

Feuerstein and v. Kostanecki (Ber., 32, 1024) assigned at first the following constitution to brazilin :—



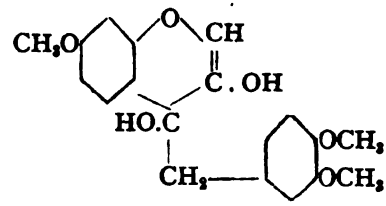
which was based upon the production from it of dihydroxypheno-γ-pyrone (Schall and Dralle) by alkaline oxidation, and of protocatechuic acid by fusion with alkali (Herzig).

It was, however, pointed out by Perkin that this formula does not account for the presence of *m*-hemipinic acid among the oxidation products of trimethylbrazilin, and Herzig and Pollak (Monatsh., 1901, 22, 207) advanced a similar criticism. On the other hand, it was suggested at the time by v. Kostanecki and Lampe (Ber., 1902, 35, 1667) that *m*-hemipinic acid was not to be regarded as an oxidation product of trimethylbrazilin itself, but that it arose from the formation, during the oxidation, of a phenanthrene or indene-derivative, which by the further action of permanganate gives this acid. Such an indene-condensation is illustrated by the following scheme, which, according to these authors, probably occurred during the formation of trimethylbrazilone from trimethylbrazilin.

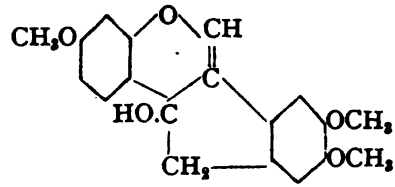
The first product of the oxidation with chromic acid will possess

the formula (1), and this is converted by the following stages into trimethylbrazilone (3)—

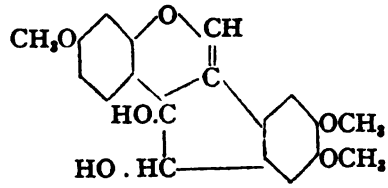
(1)



(2)

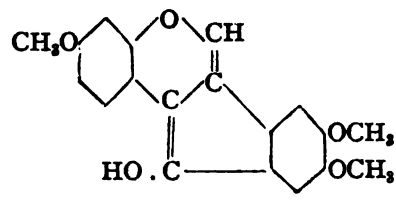


(3)



This constitution accounts in a simple manner for the formation of the anhydrotrimethylbrazilone (1), and the nitrohydroxydihydrotrimethylbrazilone (2), of Perkin, which can be represented as follows :—

(1)



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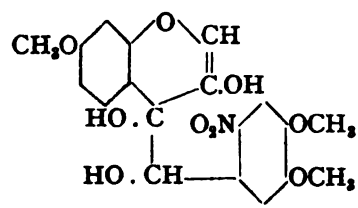
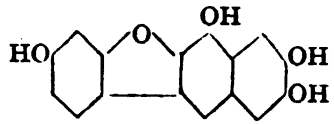


When anhydrotrimethylbrazilone is digested with hydriodic acid, *anhydrobrazilone*, $C_{16}H_{10}O_5 + H_2O$, is produced, but when trimethylbrazilone itself is treated in a similar manner, the result is of a peculiar nature. The compound $C_{16}H_6O(OH)_4$ so obtained does

not consist of brazilone, but possesses the formula (1) or (2), and on distillation with zinc-dust gives *brazan* (3) (v. Kostanecki and Lloyd, Ber., 1903, 36, 2193)—

(1)



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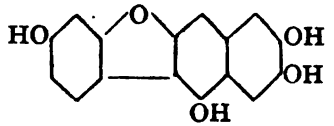

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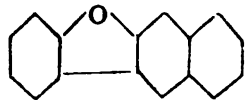
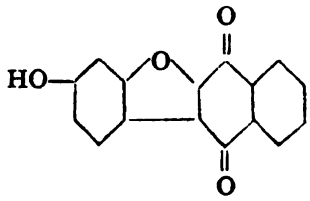
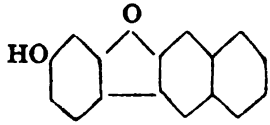


In 1899 Liebermann (Ber., 32, 924) obtained anhydro-*a*-naphthoquinone resorcin by the condensation of 2-3-dichlor-*a*-naphthoquinone with resorcin—

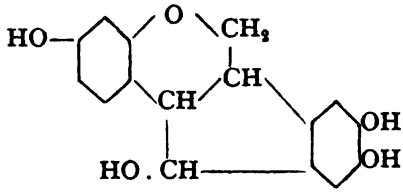


and this, according to v. Kostanecki and Lampe (Ber., 1908, 41, 2373) is 3-hydroxybrazanquinone. By reduction with hydriodic acid, this gives hydroxybrazan—



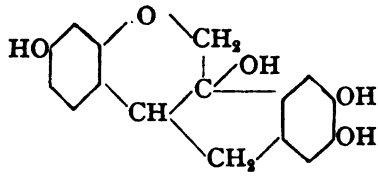
and from this latter or from the quinone itself, brazan, identical with that obtained from trimethylbrazilone, is produced by distillation with zinc-dust. Brazan crystallises in leaflets, and melts at 202°.

v. Kostanecki and Lampe (Ber., 1902, 35, 1674) considered it probable that, after all, trimethylbrazilin does contain, as found by Perkin, a nucleus which on oxidation yields hemipinic acid, and appear to have adopted the following as their final formula for brazilin :—

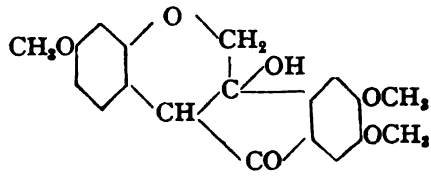


This constitution, it is evident, will still harmonise with the formulæ of trimethylbrazilone and anhydrotrimethylbrazilone given above by these authors.

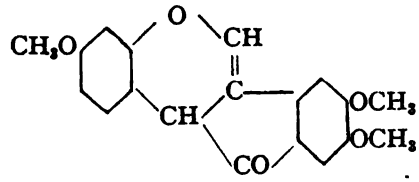
Herzig and Pollak (Ber., 1906, 39, 267) suggested the following constitution for brazilin, trimethylbrazilone, and anhydrotrimethylbrazilone:—



Brazilin.

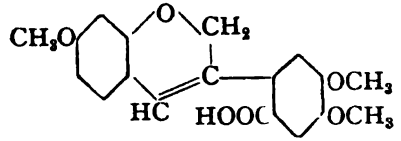


Trimethylbrazilone.

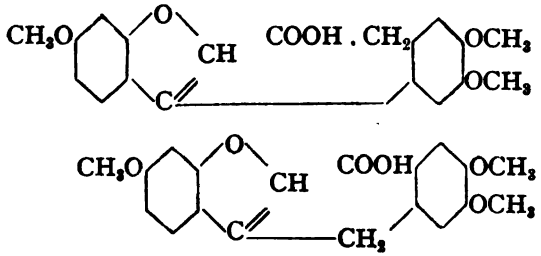


Anhydrotrimethylbrazilone.

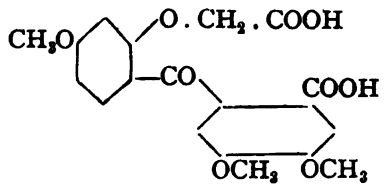
Herzig, moreover, observed (Ber., 1904, 37, 631) that trimethylbrazilone undergoes isomeric change when it is dissolved in sulphuric acid, and yields *γ-trimethylbrazilone*, $C_{16}H_9O_3(OCH_3)_3$, melting-point 170—173°, to which the formula



was assigned (Herzig and Pollak, Monatsh., 1906, 27, 743). Perkin and Robinson (*loc. cit.*) find that on oxidation with permanganate this compound gives large quantities of *2-carboxy-4-5-dimethoxy-phenylacetic acid*, $(CH_3O)_2 . C_6H_2 . (COOH) . CH_2 . COOH$, and that there can be little doubt that its true constitution is represented by one of the following formulæ:—



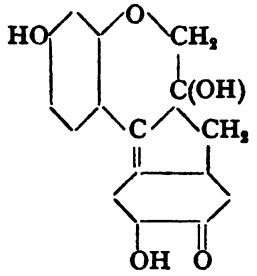
Finally, in 1906 Herzig and Pollak (Monatsh., 27, 743) considered it necessary to modify their first formula for brazilin, and arrived at the conclusion that that finally proposed by v. Kostanecki and Lampe correctly represents this colouring principle. The more recent work of Perkin and Robinson detailed above shows, however, that such a constitution cannot be correct, because it does not account for the production of brazilinic acid by the oxidation of trimethylbrazilin—



and there is every reason to consider that the formula suggested by the latter authors (p. 353) is the correct representation of the constitution (cf. also Perkin and Robinson, Chem. Soc. Trans., 1909, 95, 381) of brazilin.

Brazilein yields a *triacetyl* derivative, $C_{16}H_9O_5(C_2H_3O)_3$, yellow leaflets, melting-point 203—207° (Schall and Dralle, Ber., 23, 1434), and a *trimethyl ether*, $C_{16}H_9(OCH_3)_3O_2$, which crystallises in two modifications, melting at 160° and 178° respectively (Engels and Perkin, Chem. Soc. Proc., 1906, 22, 132). Brazilein trimethyl ether combines with formic acid, yielding a formic acid derivative which crystallises in garnet-coloured prisms, and is decomposed into its components by treatment with alcohol.

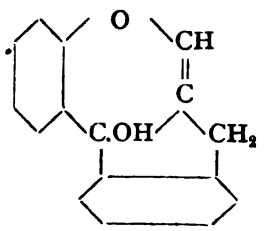
The constitution assigned to brazilein by Perkin is as follows:—



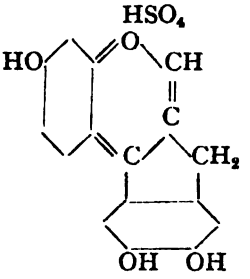
When brazilein is dissolved in sulphuric acid, and the solution is diluted with acetic acid, minute orange-red prisms of *isobrazilein sulphate*, $C_{16}H_{11}O_4 . SO_4H$, separate (Hummel and A. G. Perkin, Chem. Soc. Trans., 1882, 41, 367), and this, on treatment with alcohol, gives the basic sulphate $C_{16}H_{12}O_5(C_{16}H_{11}O_4 . SO_4H)_2$, which crystallises in red needles. Hydrochloric and hydrobromic acids at 100° give *isobrazileinchlorhydrin*, $C_{16}H_{11}O_4Cl$, and *isobrazileinbromhydrin*, $C_{16}H_{11}O_4Br$, and both compounds consist of orange-coloured prisms, which are somewhat readily soluble in water, forming a solution which contains free haloid acid. These interesting substances dye mordanted fabrics colours which are entirely different from those yielded by brazilein, and the shades which are produced, especially on calico, somewhat resemble those given by alizarin. From these haloid salts by digestion with silver oxide a substance is produced known as *isobrazilein*, which has the formula $C_{16}H_{12}O_6$, but is totally distinct from brazilein.

According to Engels, Perkin and Robinson (Chem. Soc. Trans., 1908, 93, 1140), whose paper must be consulted for the detailed account of brazilein and its derivatives, these isobrazilein salts are derived from 4-3-*indenobenzopyranol* (1), and the sulphate which is *trihydroxy*-4-3-*indenobenzopyranolanhydrohydrogen sulphate* (2) may be represented thus:—

(1)

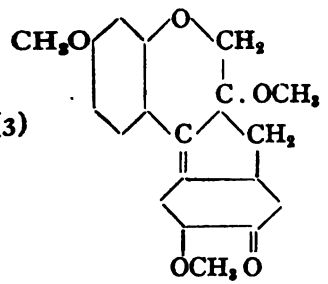


(2)

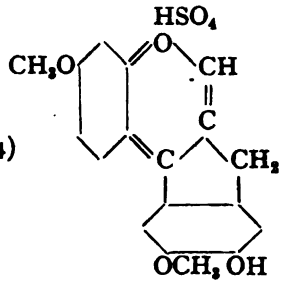


It was found, for instance, that when brazilein trimethyl ether (3) is treated with sulphuric acid, it is converted with loss of methyl alcohol into the dimethyl ether of isobrazilein sulphate (4)—

(3)



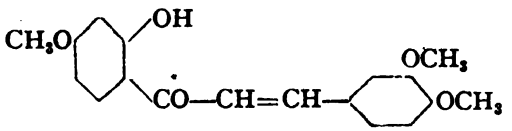
(4)



These authors assign an orthoquinonoid structure to this and similar oxonium salts.

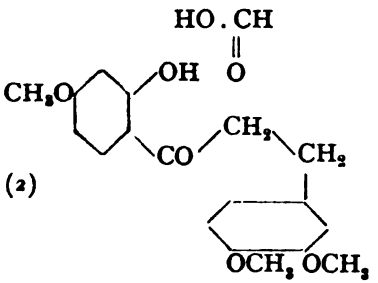
More recently Robinson (private communication), employing butein trimethyl ether, has succeeded by very simple methods in synthesising isobrazilein hydrochloride. By reducing butein trimethyl ether (1)—

(1)

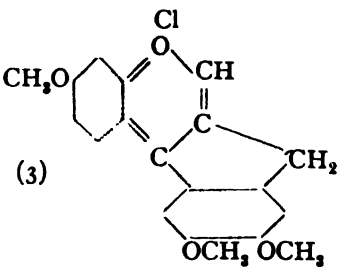


the dihydro (benzylacetophenone) compound (2) is obtained. This by digestion with an excess of absolute formic acid in presence of zinc chloride is transformed into the hydrochloride of isobrazilein trimethyl ether (3)—

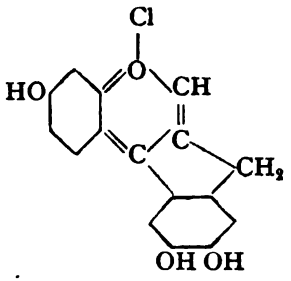
(2)



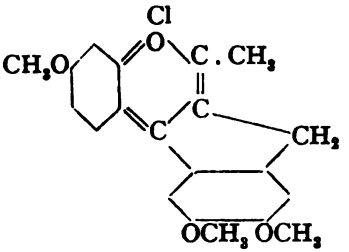
(3)



With fuming hydrochloric acid at 120—150° demethylation occurs and isobrazilein hydrochloride is produced—



By the substitution of acetic acid for formic acid in this reaction the corresponding methylisobrazilein derivative can be obtained—



The synthesis in this manner of a colouring matter so closely allied to brazilin itself by the employment of butein, a yellow dye which exists in the flowers of the *Butea frondosa* (Perkin, Chem. Soc. Trans., 1904, 85, 1459), is of exceptional interest.

The commercial preparations of Brazilwood known as Brazilwood extract and Brazilwood liquor, are prepared by boiling the ground fresh wood with water, and evaporating the decoction thus obtained to various degrees of consistency without access of air, or as rapidly and at as low a temperature as possible, e.g. in vacuum pans.

Dyeing Properties.—Before dyeing the logs, as imported, are rasped to a coarse powder, and this is then usually moistened with water and allowed to ferment for some weeks. This operation is performed in order to increase the colouring power of the wood, and there can be little doubt that a considerable quantity of the brazilin present is thereby oxidised to the colouring matter brazilein. It has been considered by some that the fresh wood contains in reality a glucoside of brazilin, which, under the influence of fermentation, is hydrolysed, but no evidence has been forthcoming in support of this suggestion.

Although still used in calico printing and in wool dyeing, Brazilwood and its allies have lost their importance, chiefly because of the fugitive character of the colours they yield. In calico printing

sappan liquor is employed for producing steam reds and pinks, the mordant used being aluminium acetate or stannic oxalate, separately or combined, together with some oxidising agent, e.g. potassium chlorate or a copper salt. It also enters into the composition of steam chocolates and certain steam colours in conjunction with other dyewood extracts. These woods have also been much used in the past along with garancine in dyeing the reds, chocolates, and other colours of cheap prints.

In wool dyeing these woods have been applied for the purpose of dyeing reds and various shades of claret and brown, the wool being previously mordanted with alum and cream of tartar or oxalic acid, or with potassium dichromate, in which case other dyewoods, e.g. logwood and old fustic, are applied in addition. The colours produced by this method are now only used to a limited extent.

In cotton dyeing, peachwood-red was formerly obtained by first preparing the cotton with tannin matter, then mordanting with a stannic salt, and finally dyeing with peachwood, sappan-wood, etc. Browns were obtained by the use of logwood in addition, with or without a final passage through a ferric salt solution (nitrate of iron). These colours are now replaced by others obtained from coal tar.

Logwood.

Logwood or Campeachy wood is one of the most important dyestuffs, and at the present time is very largely employed. Although for a long time it has successfully competed with the artificial colouring matters, its supremacy as a cotton dye has been affected to a considerable extent by the introduction of the sulphide blacks.

Logwood appears to have been first imported into Europe by the Spaniards shortly after the discovery of America, and has been cultivated in Jamaica from the year 1715. In the time of Elizabeth its employment as a dye was prohibited by Act of Parliament, and large quantities of the wood were burned, because it was said to produce fugitive colours.

It is derived from the *Hæmatoxylon campechianum* (Linn.), a tree which belongs to the family *Cæsalpiniaceæ*, and is a native of the warmer part of South America and some of the West India Islands. It also grows in the island of Mauritius, and trials indicate that this wood is of good quality (private communication).

Logwood usually comes into the market in large blocks weighing about 400 lbs. These externally are of a deep brown colour, but

internally have a much lighter tint. The best qualities come from Jamaica, Honduras, and St. Domingo, for the true Campeachy wood, at one time esteemed to be the best, is now practically exhausted.

The colouring principle of logwood, ***hæmatoxylin***, was first isolated in a crystalline condition by Chevreul (Ann. Chim. Phys., (ii.), 82, 53, 126), who obtained it by extracting the wood with ether, evaporating the extract, and digesting the residue with alcohol. After distilling off the alcohol the residue was allowed to stand in contact with water, when the hæmatoxylin separated in crystals. It may also be prepared by similarly treating commercial logwood extract which has been incorporated with a large quantity of sand (O. L. Erdmann, Annalen, 44, 292; J. pr. Chem., 26, 193; 36, 205; 75, 318). For this purpose ether containing water is preferable (Hesse, Annalen, 109, 332). It is, however, more easily obtained from the dark-coloured crusts which slowly separate when concentrated logwood liquor stands for some time in a cool place. The crude mass is ground to a fine powder, extracted repeatedly with ether, the ethereal solution evaporated, and the residue left in contact with water, when dark-coloured crystals separate, which by recrystallisation from water containing a small quantity of sodium bisulphite, may be obtained colourless (W. H. Perkin and Yates, Chem. Soc. Trans., 1902, 81, 236).

Pure hæmatoxylin crystallises in prisms with $3H_2O$, and is sparingly soluble in cold, readily so in hot water. Its aqueous solution is coloured purple with alkalis, and this on exposure to air eventually assumes a brown tint. Hæmatoxylin is dextro-rotatory, a 1 per cent. aqueous solution having a rotation of 1·85 in a 200 mm. tube. It readily reduces salts of silver and gold, gives with alum a rose-red coloration, with iron alum a violet-black precipitate, and with neutral and basic lead acetate at first a colourless and then a blue deposit which darkens by air oxidation.

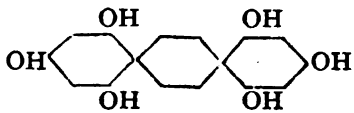
O. L. Erdmann (*loc. cit.*) was the first to submit hæmatoxylin to analysis, and proposed the formula $C_{40}H_{17}O_5$, which he subsequently altered to $C_{16}H_{14}O_6$. This latter formula was confirmed by Hesse (*loc. cit.*) and at the present day is accepted as correct.

By fusion with alkali, hæmatoxylin yields pyrogallol (Reim, Ber., 1871, 4, 331), and according to E. Erdmann and Schultz (Annalen, 216, 234) also formic acid. R. Meyer (Ber., 1879, 12, 1392) submitted hæmatoxylin to destructive distillation and considered that in this manner not only pyrogallol but also resorcinol is produced. According, however, to W. H. Perkin and Gilbody (Chem. Soc. Trans., 1902, 81, 245), no resorcinol is thus obtained.

Reim acetylated hæmatoxylin with acetyl chloride and prepared a substance which appeared to be the hexa-acetyl derivative

$$C_{16}H_8O_6(C_2H_3O)_6,$$

and as a result suggested the following constitution for this colouring principle:—



E. Erdmann and Schultz (Annalen, 1883, 216, 234) re-examined Reim's compound and showed that this was in reality a *penta-acetyl-hæmatoxylin*, $C_{16}H_9O_6(C_2H_3O)_5$, melting-point 165—166°, and that hæmatoxylin therefore contains five hydroxyl groups. This result was confirmed by the work of Herzig (Monatsh., 1894, 15, 143), who, by the action of sodium methoxide and methyl iodide on hæmatoxylin, obtained the *tetramethyl derivative*, $C_{16}H_{10}O_2(OMe)_4$, melting-point 139—140°, a substance which still contains a hydroxyl group, since on treatment with acetic anhydride it yields *acetyltetramethyl-hæmatoxylin*, $C_{16}H_9O_2(OMe)_4(C_2H_3O)$, melting-point 178 — 180°. It was thus shown that hæmatoxylin like brazilin contains an alcoholic hydroxyl group which is not methylated by means of methyl iodide and sodium methoxide under the usual conditions, and indeed it has long been considered probable that these two colouring matters are closely allied in constitution (Liebermann, Ber., 1876, 9, 1883; compare also Hummel and A. G. Perkin, Chem. Soc. Trans., 1882, 41, 373).

The following derivatives of hæmatoxylin have also been prepared: *Pentamethylhæmatoxylin*, $C_{16}H_9O(OCH_3)_5$, plates, melting-point 144—147° (Herzig); *dibromhæmatoxylin*, $C_{16}H_{12}Br_2O_6$ (Dralle, Ber., 1884, 17, 373); *penta-acetylbromhæmatoxylin*,

$$C_{16}H_8BrO_6(C_2H_3O)_5,$$

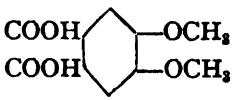
needles, melting-point 110° (Buchka, *ibid.*, 1884, 17, 685); *penta-acetyltetrabromhæmatoxylin*, $C_{16}H_5Br_4O_6(C_2H_3O)_5$ (Dralle); and *hæmatoxylinphthalein*, $C_{40}H_{20}O_{14}$ (Letts, Ber., 1879, 12, 1652).

Our main knowledge of the chemistry of hæmatoxylin and the fact that it is in reality hydroxybrazilin is due to the elaborate researches of W. H. Perkin and his pupils, and their results have arisen mainly from a study of the oxidation products of hæmatoxylin tetramethyl ether.

According to this author (Chem. Soc. Trans., 1902, 81, 1059),

tetramethylhæmatoxylin is most readily prepared by treating the solution of hæmatoxylin in alcoholic potash with methyl sulphate, a method which had previously been found serviceable by v. Kostanecki and Lampe (Ber., 1902, 35, 1669) for the production of trimethylbrazilin from brazilin.

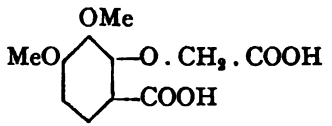
When tetramethylhæmatoxylin is oxidised with potassium permanganate (Perkin and Yates, *loc. cit.*), it yields ***m-hemipinic acid***,



an important result, because it is thus certain that hæmatoxylin like brazilin (Gilbody, Perkin and Yates, Chem. Soc. Trans., 1901, 79, 1400) contains a catechol nucleus. Consequently, whereas in the molecule of brazilin a resorcinol and a catechol nucleus occur, in hæmatoxylin pyrogallol and catechol groups are present.

In addition to *m*-hemipinic acid, large quantities of a second acid $C_{11}H_{12}O_7$, melting-point 215°, are produced. This is *2-carboxy-5 : 6-dimethoxyphenoxyacetic acid* (1)—

(1)



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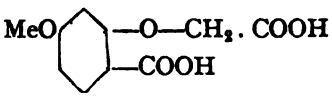


analogous to the *2-carboxy-5-methoxyphenoxyacetic acid* (2) which was obtained in a similar manner from brazilin trimethyl ether (see BRAZILWOOD).

Finally, from the product of the oxidation a third compound ***hæmatoxylinic acid***, $C_{20}H_{20}O_{10}$, melting-point 180°, was isolated. This on reduction with sodium amalgam is converted quantitatively into an acid $C_{20}H_{20}O_9$, which is a monobasic lactonic acid, and it is therefore evident that the latter is produced in two stages thus:—

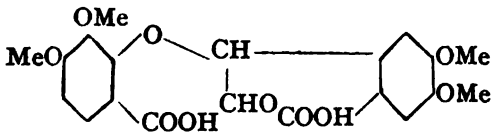
$$C_{20}H_{20}O_{10} + 2H = C_{20}H_{22}O_{10}$$

Hæmatoxylinic acid. Dihydrohæmatoxylinic acid.

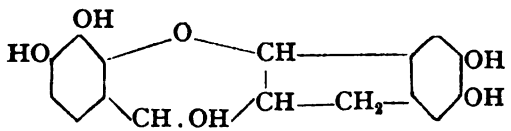
$$C_{20}H_{22}O_{10} - H_2O = C_{20}H_{20}O_9$$

Lactone of dihydrohæmatoxylinic acid.

The constitution at first assigned to hæmatoxylinic acid by these authors was as follows:—

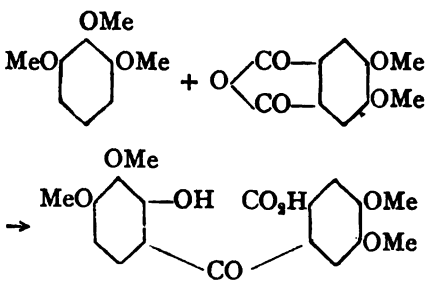


but this, and the corresponding hæmatoxylin formula—



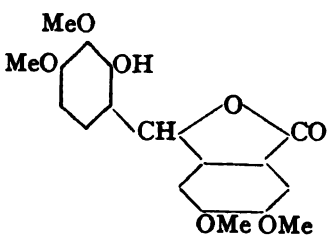
were subsequently modified, as the result of the synthesis of the lactone of dihydro-hæmatoxylinic acid referred to above (Perkin and Robinson, Chem. Soc Trans., 1908, 93, 492).

When aluminium chloride reacts with a mixture of pyrogallol trimethyl ether and *m*-hemipinic anhydride, *2′-hydroxy*-3′ : 4′ : 4 : 5-*tetramethoxybenzoylbenzoic acid* is produced:—

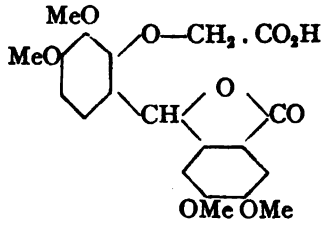


This ketonic acid is then converted by reduction with sodium amalgam into *2-m-meconyl*-5 : 6-*methoxyphenol* (1), which by treatment with chloracetic acid and sodium hydroxide gives the lactone of dihydrohæmatoxylinic acid (2).

(1)

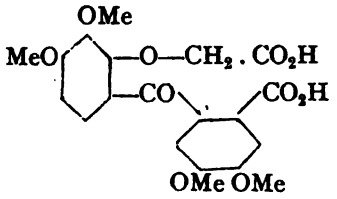


(2)

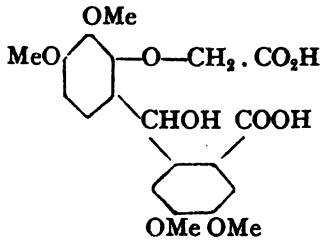


Consequently, the formulæ of hæmatoxylinic acid (3) and of dihydrohæmatoxylinic acid (4) are thus represented—

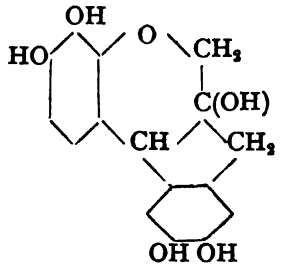
(3)



(4)

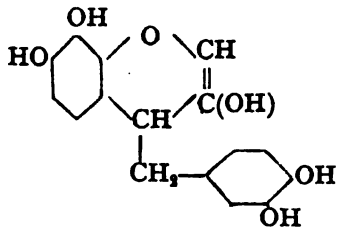


From these facts the constitution of hæmatoxylin itself naturally follows:—

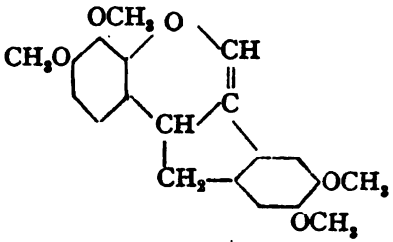


and this is identical with that which Pfeiffer (Chem. Zeit., 1904, 3, 380) from theoretical considerations suggested as possible.

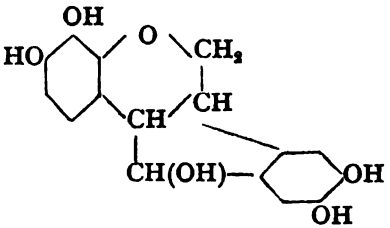
Other constitutional formulæ have been assigned to hæmatoxylin, of which that of Bollina, v. Kostanecki and Tambor (Ber., 1902, 35, 1678), analogous to the brazilin formula of Feuerstein and v. Kostanecki (Ber., 1899, 32, 1024), is of interest—



It was, however, evident that such an expression does not account for the production of *m*-hemipinic acid or 2-carboxy-5 : 6-dimethoxy phenoxyacetic acid by the oxidation of hæmatoxylin tetramethyl ether. On the other hand, v. Kostanecki and Lampe (Ber., 1902, 35, 1667) at first suggested that previous to the degradation of the methyl ether by oxidation with permanganate an internal linkage is produced, with production of the following compound :—



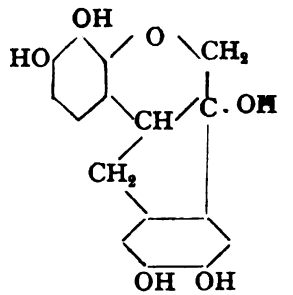
These authors ultimately considered, as W. H. Perkin contended, that a *m*-hemipinic residue is contained in hæmatoxylin tetramethyl ether, and as a result proposed the following modification of their formula for this colouring matter :—



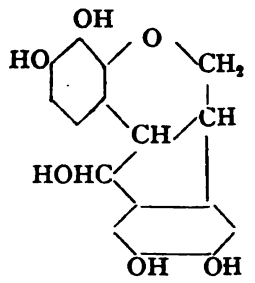
Hæmatoxylin.

Again, Herzig and Pollak (Monatsh., 1906, 27, 743; Ber., 1906, 39, 267), in a criticism of the earlier formula of Gilbody, Perkin and Yates (*loc. cit.*), suggested, among others, two possible constitutions for brazilin, the second of which is identical with that of v. Kostanecki and Lampe (see above), and which applied to hæmatoxylin, are thus represented :—

(1)



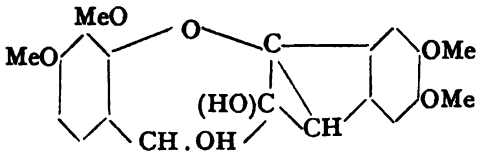
(2)



These formulæ of v. Kostanecki and Lampe and Herzig and Pollak cannot, however, be correct, as they do not account for the formation of hæmatoxylinic acid by the oxidation of tetramethylhæmatoxylin with permanganate (Gilbody, Perkin and Yates, *loc. cit.*).

Herzig (Monatsh., 16, 906) submitted acetyltetramethylhæmatoxylin to oxidation with chromic acid and obtained a new product, which on hydrolysis gave *tetramethyldehydrohæmatoxylin*, $C_{16}H_5 . O(OMe)_4OH$. This latter, on acetylation, yielded *acetyltetramethyldehydrohæmatoxylin*, $C_{16}H_5O(OMe)_4(OC_2H_3O)$, and by methylation *pentamethyldehydrohæmatoxylin*.

W. H. Perkin (Chem. Soc. Trans., 1902, 81, 1057) oxidised tetramethylhæmatoxylin with chromic acid, and obtained a substance *tetramethylhæmatoxylone*, $C_{16}H_6O(OMe)_4(OH)_2$, corresponding in all its reactions with trimethylbrazilone. For this, at that time, the formula

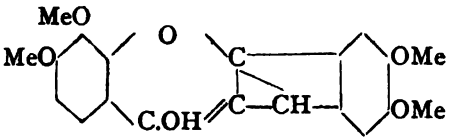


was proposed. In addition to this compound, 2-carboxy-5-6 dimethoxyphenoxyacetic acid and *m*-hemipinic acid were also produced during the oxidation. When digested with acetic anhydride, tetramethylhæmatoxylone gives *acetylanhydrotetramethylhæmatoxylone*,

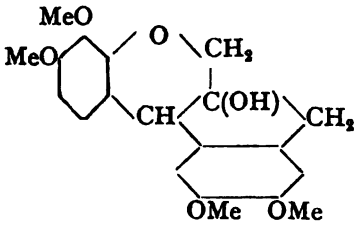
$$C_{16}H_5O(OMe)_4(OC_2H_3O),$$

evidently identical with Herzig's acetyltetramethyldehydrohæmatoxylin referred to above.

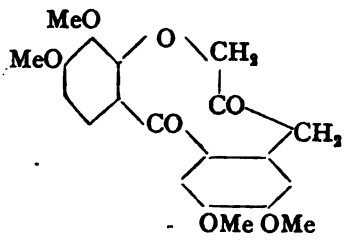
By hydrolysis this compound gave anhydrotetramethylhæmatoxylone, $C_{16}H_5O(OMe)_4OH$—



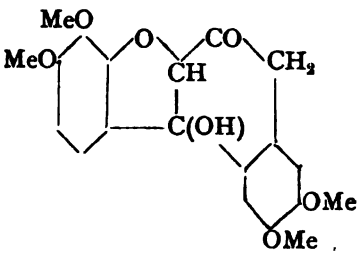
In a later paper Perkin and Robinson (Chem. Soc. Trans., 1908, 498) discarded these expressions and assigned to tetramethylhæmatoxylone the constitution given below. These authors consider that during the oxidation of tetramethylhæmatoxylin with chromic acid, a destruction of the central linkage occurs, and the unstable diketone which is thus formed undergoes aldol condensation with the production of tetramethylhæmatoxylone—



Tetramethylhæmatoxylin.



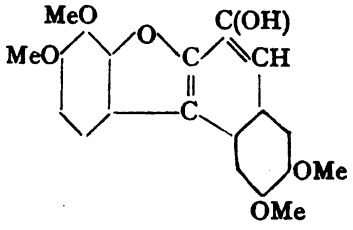
Diketone.



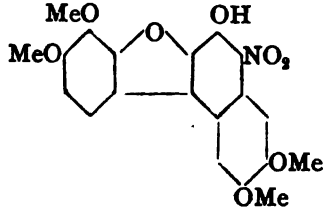
Tetramethylhæmatoxylone.

This formula indicates that tetramethylhæmatoxylone is a derivative both of coumaran and tetrahydronaphthalene.

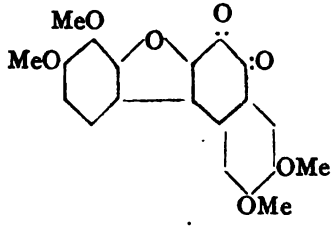
The formation of anhydrohæmatoxylone by means of acetic anhydride (*loc. cit.*) is due to the elimination of water from the aldol grouping in tetramethylhæmatoxylone, and the constitution thus given to this substance represents it as a derivative of β-naphthol, with which indeed it has many properties in common—



When acetylanhydrotetramethylhæmatoxylone is treated with nitric acid it readily reacts with the formation of the mononitro compound (Perkin and Robinson, *ibid.*, 1909, 384)—



and from this substance by reduction with zinc-dust and hydrochloric acid the corresponding amino derivative is produced. This, when oxidised by ferric chloride, yields *tetramethoxy-a-brazanquinone* (compare v. Kostanecki and Rost, *loc. cit.*)—

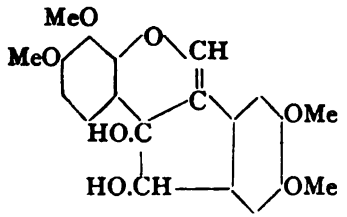


That this substance is an ortho-quinone is shown by its behaviour with *o*-tolylenediamine with which it condenses with formation of a characteristic quinoxaline. On reduction, the quinone is converted into the corresponding *dihydroxy* derivative.

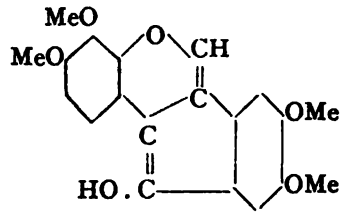
v. Kostanecki and Rost (Ber., 1903, 36, 2202), on the other hand, proposed for the tetramethylhæmatoxylone (1) and anhydrotetramethylhæmatoxylone (2) of Perkin the following expressions which

harmonised with their suggested constitution for hæmatoxylin (*loc. cit.*)—

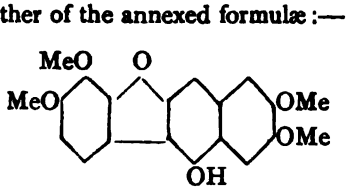
(1)



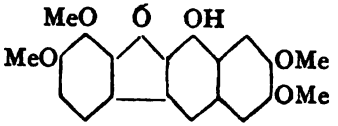
(2)



According to these authors, when tetramethylhæmatoxylone is treated with alcoholic sulphuric acid, a new compound (1′ or 4′) *hydroxy*-3 : 4 : 6′ : 7′-*tetramethoxybrazan* is formed, which is represented by one or other of the annexed formulæ:—

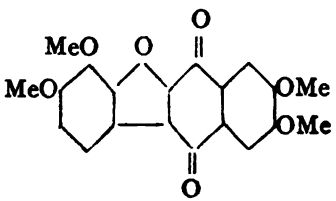


or

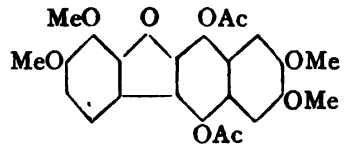


Oxidation with chromic acid converts this substance into 3 : 4 : 6′ : 7′-*tetramethoxybrazanquinone* (1), which by reduction and acetylation yields 3 : 4 : 6′ : 7′-tetramethoxy (1′ : 4′) diacetoxybrazan (2)—

(1)

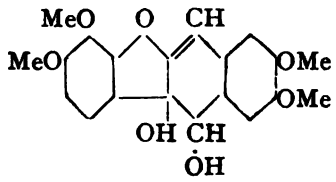


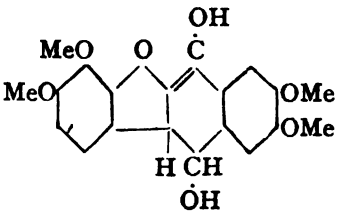
(2)



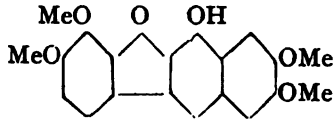
When distilled with zinc-dust, both hydroxytetramethoxybrazan and tetramethoxybrazanquinone yield *naphthalene*.

Herzig and Pollak (Ber., 1904, 37, 631) also found that cold concentrated sulphuric acid converts tetramethylhæmatoxylone into an isomeric compound *ψ-tetramethylhæmatoxylone*, and suggested the following formulæ as applicable to this substance—

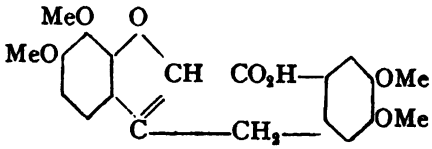




This by loss of water gives *β-anhydrotetramethylhæmatoxylone*, which is identical with v. Kostanecki and Rost's hydroxytetramethoxybrazan—

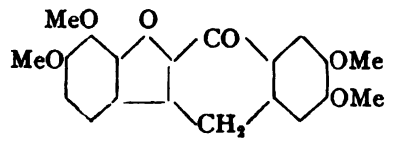


Perkin and Robinson (*loc. cit.*), as the result of a study of the work of Herzig and Pollak, have, however, shown that ψ-tetramethylhæmatoxylone is in reality a monobasic acid, and possesses the following constitution :—

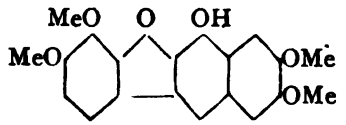


This, by elimination of water, passes into the compound (1) and then by intramolecular change into hydroxytetramethoxybrazan (2):—

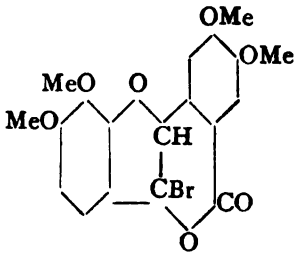
(1)



(2)



When ψ-tetramethylhæmatoxylone is treated with potassium hypobromite a colourless precipitate soon separates. This crystallises in almost colourless prisms or needles, and possesses the constitution of a *tetramethoxycumarono-iso-coumarinhydrobromide*:—*



For the theoretical considerations involved in the production of this interesting substance the original paper should be consulted.

Hæmatein.—When oxidised under suitable conditions, hæmatoxylin readily passes into the colouring matter hæmatein, according to the equation $C_{16}H_{14}O_6 + O = C_{16}H_{12}O_6 + H_2O$.

Hæmatein was first produced by O. L. Erdmann (*loc. cit.*) by passing air through an ammoniacal solution of hæmatoxylin, and subsequently acidifying with acetic acid.

Erdmann and Schultz (*loc. cit.*) who adopted a somewhat similar procedure, succeeded in isolating hæmatein in leaflets which possessed a metallic lustre. Reim, on the other hand (Ber., 1871, 4, 331), treated an ethereal solution of hæmatoxylin with a little concentrated nitric acid.

By extracting "aged" logwood with ether, Halberstadt and Reis

* ψ-trimethylbrazilone behaves analogously.

(Ber., 1881, 14, 611) obtained 1 per cent. of a very pure crystalline hæmatein.

Hummel and A. G. Perkin (Chem. Soc. Trans., 1882, 41, 373) exposed an ammoniacal solution of logwood extract to the air for two or three days. The precipitated ammonia compound of hæmatein was collected, dissolved in water, dilute acetic acid added, and the mixture digested on the water-bath to dissolve as much as possible of the suspended amorphous hæmatein. The clear liquid after partial evaporation deposited crystals of the colouring matter, possessing a yellowish-green iridescence, and having the composition $C_{16}H_{12}O_6$.

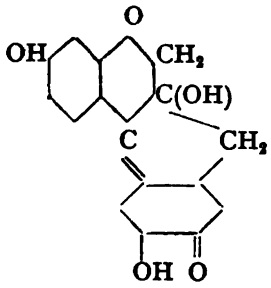
According to Mayer (Chem. Zentr., 1904, 1, 228), hæmatein may also be prepared by oxidising hæmatoxylin in aqueous solution with sodium iodate.

Engels, W. H. Perkin and Robinson (Chem. Soc. Trans., 1908, 93, 1140) passed air for six hours through a solution of 15 grams of hæmatoxylin, dissolved in a solution of 15 c.c. of concentrated ammonia in 150 c.c. of water. The product of the oxidation was added in a thin stream to dilute acetic acid (250 c.c. of 10 per cent.) heated on the water-bath, when hæmatein separated in crystals.

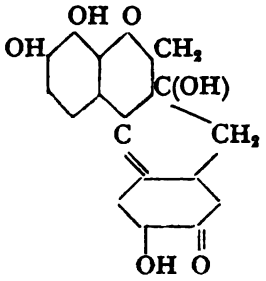
Hæmatein is very sparingly soluble in water and the usual solvents. Alkalis dissolve it readily; ammonia dissolves it with a brown-violet colour, whilst its strong alkaline solution has a rich purplish-blue colour. On exposure to air the colour of these alkaline solutions gradually becomes red and finally brown, the colouring matter being destroyed. By addition of potassium acetate to the boiling alcoholic solution of hæmatein, the monopotassium salt $C_{16}H_{11}O_6K$ is deposited (A. G. Perkin, Chem. Soc. Trans., 1899, 75, 443).

Sulphurous acid or sodium bisulphite solution converts hæmatein into a colourless addition product, readily soluble in water, but no reduction hereby appears to occur, as on boiling the solution or by addition of acid hæmatein is precipitated. With zinc and hydrochloric acid or with stannous chloride and caustic soda, a solution of hæmatein is decolorised, but on standing the liquid regains its former tint.

It has long been considered that hæmatein is hydroxybrazilein, and this has now been clearly proved by a study of the behaviour of both hæmatein and brazilein with reagents under similar circumstances. This relationship is at once evident from a comparison of the following formulæ (Engels, Perkin, and Robinson) :—



Brazilein.

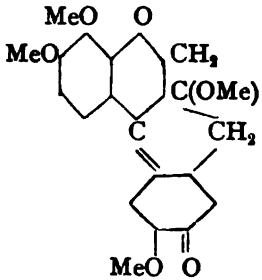


Hæmatein.

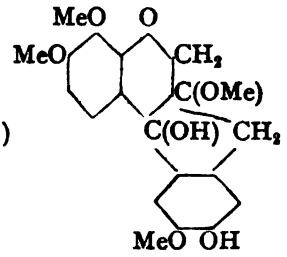
When hæmatein is methylated by means of alkali and methyl sulphate, the product consists essentially of tetramethylhæmatein and pentamethyldihydrohæmateinol.

Tetramethylhæmatein (1) crystallises in amber prisms, and when digested with dilute potassium hydroxide is converted by the addition of water into *tetramethyldihydrohæmateinol* (2), yellow prisms—

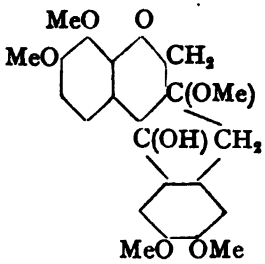
(1)



(2)



Pentamethyldihydrohæmateinol,



the second product of the reaction, crystallises in yellow plates, and is also produced when tetramethyldihydrohæmateinol is methylated with methyl sulphate and alkali.

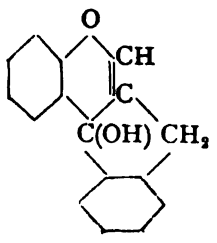
In the year 1882 Hummel and A. G. Perkin (Chem. Soc. Trans., 41, 367) observed that hæmatein and also brazilein are converted by the action of mineral acids into orange or red salts, from which the original colouring matters could not be regenerated.

When hæmatein is dissolved in cold sulphuric acid, a reddish-brown solution is produced from which, by cautious addition of acetic acid, minute orange-coloured prisms of *acid isohæmatein-sulphate*, $C_{16}H_{12}O_5SO_4$, are deposited. The reaction may be represented thus: $C_{16}H_{12}O_6 + H_2SO_4 = C_{16}H_{12}O_5SO_4 + H_2O$. This substance, when left in contact with 80 per cent. alcohol, is gradually transformed, with loss of sulphuric acid, into a new compound crystallising in orange-red plates possessing a strong metallic lustre and to which the formula $(C_{16}H_{12}O_6)_2C_{16}H_{12}O_5SO_4$ was assigned. On the other hand, hydrochloric and hydrobromic acids in sealed tubes at 100° convert hæmatein respectively into *isohæmatein chlorhydrin*, $C_{16}H_{11}O_5 . Cl$, and *isohæmatein bromhydrin*, $C_{16}H_{11}O_5Br$, which crystallise in orange-red needles.

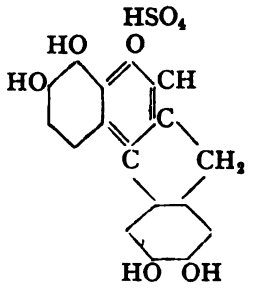
If to an aqueous solution of *iso*hæmatein chlorhydrin or bromhydrin silver hydroxide is added to remove the halogen, a solution of *isohæmatein* is obtained, which on evaporation leaves this substance as an amorphous mass possessing a green metallic lustre. *Iso*hæmatein and its salts dissolve in solutions of the alkaline hydroxides with a red-violet colour which is easily distinguished from the corresponding blue-violet solution of hæmatein; moreover, the dyeing properties of these compounds and hæmatein differ considerably. Thus the *iso*hæmatein derivatives give, on cotton mordanted with alumina, a dull red inclining to chocolate, with strong iron a black, and with mixed alumina and iron a full chocolate. Again, the tinctorial power of these compounds is much greater than that of the original hæmatein, and the colours are much faster.

As the result of the investigation of a large number of pyranol salts (W. H. Perkin, Robinson, and Turner, Chem. Soc. Trans., 1908, 93, 1085), it seems certain that these hæmatein salts are derivatives of 4 : 3-*indenobenzopyranol* (1), and that *iso*hæmatein sulphate possesses the constitution (2)—

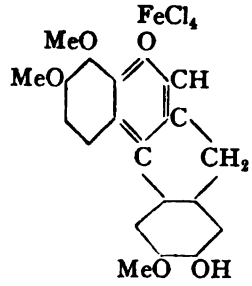
(1)



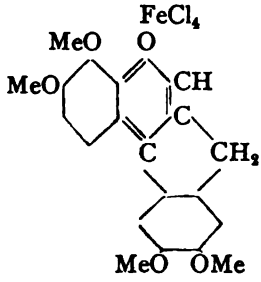
(2)



*Iso*hæmatein chlor- and bromhydrins are formulated similarly. Thus from tetramethylhæmatein, Engels, Perkin, and Robinson (*loc. cit.*) have prepared 5′-*hydroxy*-7 : 8 : 4′-*trimethoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *anhydroferrichloride*—



which crystallises from acetic acid in well-defined elongated prisms. Pentamethyldihydrohæmateinol, on the other hand, gives 7 : 8 : 4′ : 5′-*tetramethoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *anhydroferrichloride*—



Before being used by the dyer, logwood is reduced to chips or powder, and these products are known as "chipped," "rasped," or "ground" wood. When first cut down the wood has a pale yellow colour and contains only hæmatoxylin, but during transport or storage this colour gradually deepens owing to a surface oxidation of the hæmatoxylin into hæmatein. Formerly, and even to some extent at the present time, it was the practice to submit the chipped or rasped logwood to what is known as the "ageing" process, in order to facilitate the hæmatein formation. This consists in wetting the wood thoroughly with water, then forming it into heaps, 4 to 5 feet high, in large airy chambers. Very soon the mass begins to ferment, which is indicated by a rise of its internal temperature, the wood gradually darkens in colour, and during the operation the mixture is repeatedly turned over and remixed in order to avoid too vigorous a fermentation and to obtain an even result. Constant

attention is necessary during this "ageing" process, for if the reaction is allowed to proceed too far, a portion of the colouring matter is destroyed, and "burnt" or "over-aged" wood is produced. In order to expedite this operation, the use of various oxidising agents has been suggested; a sprinkling of the wood with ammonia has been said to exercise a beneficial result; but, on the other hand, such processes are best avoided, for it is difficult under these circumstances to control the reaction and prevent an over-oxidation.

Latterly this ageing operation has been less in vogue, not only on account of the increased employment of logwood extract, but because it is now recognised that where the mordant employed for dyeing purposes can exert an oxidising action, this preliminary treatment is unnecessary. Formerly, logwood blacks on wool were produced by means of an iron mordant, but this is now largely replaced by the use of potassium dichromate, which provides a mordant possessing the power of converting at least a portion of the hæmatoxylin into hæmatein.

Logwood extract is now prepared in enormous quantity not only in this country but also in Jamaica in the neighbourhood of the logwood plantations, and in the latter case an economy is naturally effected in the carriage of some varieties of the extract rather than that of the more bulky wood to this and other countries. Logwood extract is almost invariably prepared from the "unaged" wood, because whereas hæmatoxylin is readily soluble in water, hæmatein is not. On this account, an aged wood is difficult to exhaust. For the manufacture on the large scale, two processes are in vogue known respectively as the "American" and "French" methods. These differ merely in the manner in which the wood is lixiviated, for this is carried out by the French process in open pans with warm or boiling water, whereas in the American process, closed vessels are used in which steam at from 15 to 30 lb. pressure is employed. In both cases the liquid is afterwards concentrated, preferably in vacuum pans, and the product is sold at about 15° Tw. as *logwood liquor*, at 51° Tw. as *logwood extract*, or in the solid condition as *solid logwood extract*. As a rule, it is considered that the extract made at the lower temperature gives the brighter shade.

Certain processes are in use for the "ageing" of "logwood liquor," that is the conversion of the dissolved hæmatoxylin into hæmatein. For this purpose the following methods have been suggested: (*a*) treat the logwood liquor with bleaching powder solution; (*b*) half neutralise with alkali or ammonia and blow air or oxygen through the liquid; (*c*) employ air or oxygen for this purpose with-

out the addition of alkali; (*d*) boil with manganese dioxide (Weldon mud) and filter. Interesting also in this respect is the patented process of Haak (Chem. Zentr., 1905, ii., 867), who treats the extract with sodium nitrite.

A very important product more recently introduced is the so-called crystalline *hæmatein paste*, which is a treacly extract containing in suspension minute crystals of hæmatein. The details of the preparation of this material, which appears to have been first introduced from Jamaica, although now also manufactured in this country, are kept secret. For experimental purposes, this paste may be employed as the source of a comparatively pure hæmatein, which can be isolated from it by dilution with glacial acetic acid and subsequent filtration (private communication).

Logwood and its extracts are enormously employed for the dyeing of blacks on silk, wool, and to a less extent with cotton, chiefly in conjunction with iron and chromium mordants. It also enters into the composition of numerous compound shades.

Bastard Logwood.—During the past few years the growers of logwood in Jamaica have been greatly disturbed by the apparent increase on their properties of an unmerchantable variety of the tree known as "bastard" logwood. Bastard logwood is practically devoid of hæmatoxylin, but contains instead a yellowish-green pigment which, when admixed with the commercial extract, reduces its characteristic tinctorial properties. Chips of the bastard logwood present a yellow, pale pink, white, or even chocolate coloured surface instead of the dark red or purple-bronze tinted colour of the best Jamaican or Mexican logwoods of commerce.

So similar are the trees of the "true" and the "bastard" logwood, that it is frequently impossible to decide whether a tree is really a "mulatto" or not. When first cut a bastard tree is frequently dark enough internally to indicate that it is a good red-wood tree, but instead of darkening with age, as all the best wood does, it remains the same colour or becomes lighter rather than darker.

Chemical tests readily distinguish between the red and bastard wood, for whereas alkaline solutions turn an extract of true logwood a purple colour, with a bastard extract the shade of yellow is merely deepened. Again, mineral acids turn aqueous extracts of true logwood orange to bright red, whereas a bastard extract is not thereby affected.

Dyeing trials, employing stripe mordanted calico, are also serviceable, because, in the case of the bastard variety, the aluminium mordant remains practically colourless.

HÆMATOXYLON AFRICANUM.

The genus hæmatoxylon has hitherto been represented by only one species, the *H. campeachianum*, and the recent discovery of a South African species is of particular interest. This, now termed the *H. africanum*, was found among the rocks at Holoog in Great Namaqualand by Dr. H. H. W. Pearson in February, 1909, during the Percy Sladen Memorial Expedition in South-West Africa, 1909. It consists of a shrub 1—1·5 metres tall, the flowers of which are yellow, and the leaves smaller than those of the *H. campeachianum* (Stephens, Trans. Roy. Soc. S. Africa, 1913, iii., 2, 255).

Stems of this plant sent to England for examination were covered with a thin brownish bark, and varied from ½—1¼ inches in diameter, and from 11—16 inches in length. Cut transversely they were seen to consist mainly of a reddish-brown core surrounded by an almost colourless layer of wood, and this core, as is the case with logwood itself, darkened somewhat on exposure to air and became of a richer colour. When ground, the ochre-coloured powder is of a much lighter tint than either ground logwood or Brazil-wood.

The aqueous extract of the ground wood gives in comparison with those obtained from logwood and Brazil-wood the following colour tests:—

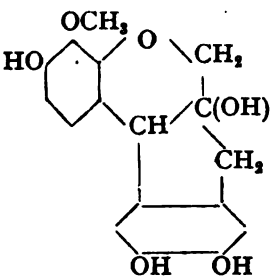
	H. africanum.	Brazil-wood.	Logwood.
NaOH . .	Pink.	Crimson.	Deep red-violet.
$FeCl_3$ . .	Brown.	Deep brown.	Purplish-black.
$Pb(Ac)_2$ . .	Pale pink almost colourless precipitate.	Pink precipitate.	Deep blue precipitate.

The alkaline extract of the *H. africanum* on boiling deepens considerably in colour and possesses a faint greenish fluorescence, and this property is also exhibited by the corresponding extract of Brazilwood.

Dyeing trials with both the *H. africanum* (170 per cent.) and Brazilwood (40 per cent.) employing mordanted woollen cloth gave the following shades:—

	Cr.	Al.	Cu.	Sn.	Fe.
H. africanum	Red-brown-violet.	Dull bluish-red.	Brown.	Very pale brown.	Dull purple.
Brazilwood .	Red-violet.	Bluish-red.	Claret-brown.	Red-brown very pale.	Blue-violet.

The *H. africanum*, therefore, differs from logwood in that the colouring principle it contains is not hæmatoxylin, but a substance which somewhat closely resembles brazilin in its general properties. It is a much poorer dyestuff than Brazilwood and on this account is of no technical importance, but should it eventually prove to contain brazilin, the matter is of special interest in view of the connection between this latter and hæmatoxylin which has been shown to exist by W. H. Perkin and his co-workers (*loc. cit.*). The slight difference in the properties of the *H. africanum* and Brazilwood may be due to certain impurities in the former dyestuff not possessed by the latter, but on the other hand a methyl ether of hæmatoxylin of the type



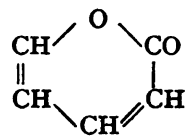
will without doubt dye shades of an almost identical character with those given by brazilin itself (Perkin, J. Soc. Dyers, 1918, 34, 99).

CHAPTER X.

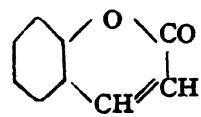
α-PYRONE OR COUMARIN GROUP.

Daphnetin.

THOUGH colouring matters containing the γ-pyrone nucleus are naturally prolific, this is not the case with those containing the *a*-pyrone grouping—



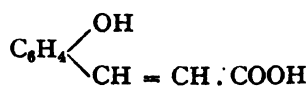
and indeed but one member of this series, namely daphnetin, has at present been isolated. This is somewhat remarkable, for though coumarin or pheno-*a*-pyrone,



which is to be regarded as the mother substance of this class, can only yield a very limited number of hydroxy compounds having tinctorial property, the introduction of phenyl or other groupings into the molecule, as in the case of the γ-pyrone compounds previously described, obviously much increases its possibilities in this respect. Compounds of this type have indeed been synthetically prepared and are described below.

The literature referring to coumarin and its derivatives is too voluminous to be given in any detail here, and a brief résumé of those points immediately bearing on the subject of this volume can only be dealt with.

Coumarin itself, which occurs in the Tonka bean and in numerous other natural products, is the lactone of *o*-cumaric (*o*-hydroxycinnamic) acid—



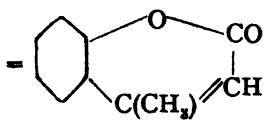
It was first artificially prepared by the late Sir W. H. Perkin from salicylic aldehyde, acetic anhydride, and sodium acetate—

$$C_6H_5COH + CH_3.COONa = C_6H_5CH = CH.COONa + H_2O,$$

the sodium *o*-cumaratè thus obtained passing on acidification into coumarin.

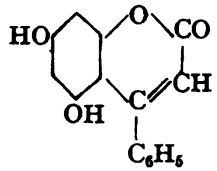
Pechmann and Duisberg (Ber., 1883, 16, 2119) synthesised coumarins and hydroxy-coumarins substituted in the side chain by the interaction of aceto-acetic ether, or benzoyl acetic ether, with phenols in the presence of dehydrating agents thus—

$$C_6H_5OH + CH_3.CO.CH_2.COOEt$$



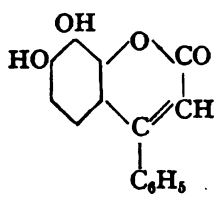
$$+ H_2O + EtOH$$

Such a method was also employed by v. Kostanecki and Weber (Ber., 1893, 26, 2906) in the synthesis of a *m*-dihydroxyphenyl coumarin—



from benzoyl acetic ester and phloroglucinol, and it appeared possible at that time that chrysin, the colouring matter of poplar buds, now known, however, to be in reality a dihydroxyflavone, possessed this structure.

In the same way also pyrogallol and benzoyl acetic ester give β-phenyl daphnetin—



This consists of faintly yellow needles, soluble in alkaline solutions with a red colour which dye with aluminium mordanted fabrics a bright yellow shade.

Coumarin forms oxonium compounds, and though itself sparingly soluble in water readily dissolves in concentrated hydrobromic and

hydrochloric acid with the formation of the corresponding salts. The unstable *hydrobromide* thus obtained was first isolated by Ebert (Annalen, 1884, 226, 347), and the following compounds of this class have been described by Morgan and Micklethwait (Chem. Soc. Trans., 1906, 89, 863).

Coumarin platinichloride, $C_{36}H_{24}O_8$, H_2PtCl_6, $4H_2O$, yellow needles, *C. aurichloride*, $4C_9H_6O_2$, $AuCl_4$, $4H_2O$, *C. cobalticyanide*, $3C_9H_6O_2$, $H_3Co(CN)_6$, $3H_2O$, colourless crystalline precipitate, and *C. hydriodide periodide*, $4C_9H_6O_2$, HI, I_3, dark green needles.

Daphnetin.

Daphnetin is present in the form of its glucoside *daphnin* in the bark of the *Daphne alpina* (Linn.) and *D. mezereum* (Linn.).

The concentrated alcoholic extract is digested with boiling water, filtered, and treated with lead acetate solution. The precipitate is removed, basic lead acetate added to the filtrate, the lead compound of the glucoside decomposed with sulphuretted hydrogen, and the solution evaporated (Zwenger, Annalen, 115, 8).

Daphnin, $C_{15}H_{16}O_9$, $2H_2O$, crystallises in prisms, melting at 200°, and dissolves in alkaline solutions with a yellow colour. It is hydrolysed by boiling dilute acids with formation of daphnetin and glucose, $C_{15}H_{16}O_9 + H_2O = C_9H_6O_4 + C_6H_{12}O_6$.

Daphnetin, $C_9H_6O_4$, forms pale yellow needles, is soluble in alkalis with a yellow colour, and gives a yellow precipitate with lead acetate solution. On acetylation, a *diacetyl*-derivative,

$$C_9H_4O_4(C_2H_3O)_2,$$

is obtained, and by means of ethyl iodide a *diethyl* ether,

$$C_9H_4O_2(OEt)_2,$$

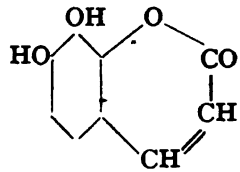
is produced. When daphnetin diethyl ether is boiled with caustic soda solution, the diethyl ether of *daphnetinic acid*,

$$(OEt)_2C_6H_2\begin{cases}OH\\CH = CH\,.\,COOH\end{cases}$$

is produced in the form of its sodium salt, which when ethylated gives the *triethyl* derivative—

$$(OEt)_2C_6H_2\begin{cases}OEt\\CH = CH\,.\,CO_2H\end{cases}$$

By oxidising daphnetinic acid triethyl ether *triethoxybenzaldehyde* is formed, which is readily converted into triethoxybenzoic acid. The silver salt of this acid, when destructively distilled, gives pyrogallol triethyl ether. Daphnetin is accordingly a *dihydroxycoumarin*, and has the following constitution :—



(Will and Yung, Ber., 1884, 17, 1081).

It has been synthetically prepared by heating pyrogallol with malic acid in the presence of sulphuric acid (Pechmann, Ber., 17, 933), $C_4H_6O_5 + C_6H_3(OH)_3 = C_9H_6O_4 + CO_2 + 2H_2O + H_2$, and by the condensation of pyrogallic aldehyde with sodium acetate (Gattermann and Koebner, Ber., 1899, 32, 287)—

$$C_6H_2(OH)_3 . CHO + CH_2 . COOH = C_9H_6O_4 + 2H_2O$$

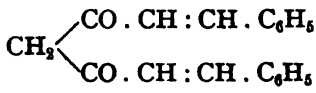
Daphnetin is a yellow colouring matter, and gives with mordanted woollen cloth the following shades :—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Olive-yellow.	Pale olive-yellow.	Very pale yellow.	Olive-black.

(Perkin and Wilson, Chem. Soc. Trans., 1903, 83, 134).

CHAPTER XI.

DICINNAMOYL METHANE GROUP.



TURMERIC.

TURMERIC (*Indian saffron; Terra merita*).—The so-called turmeric root of commerce is the underground stem or rhizome of *Curcuma longa* (Linn.), or of various species of *Curcuma*—e.g. *C. tinctoria*, *C. viridiflora* (Roxb.), etc. These plants, belonging to the *Scitamineæ*, are indigenous to Southern Asia, and are there largely cultivated, being exported from China, Madras, Bengal, Java, Malabar, Batavia, and Barbadoes. Those varieties which are derived from the central rhizomes are more or less round (*Curcuma rotunda*, Linn.), while the lateral rhizomes are long and finger-shaped (*C. longa*). When of good quality these commercial varieties are hard, and possess a dull, waxy, resinous fracture, the external colour being yellowish-grey, and internally orange-brown, but producing, when ground, a somewhat bright yellow powder, having a strong characteristic odour and a peppery bitter taste.

The rhizome of *Canna speciosa*, a West African plant, is said to be exactly similar to East Indian turmeric in taste, smell, and chemical reactions (Daniell, Pharm. J., 19, 258). It is cultivated in Sierra Leone, and furnishes the so-called "African turmeric".

According to Pelletier and Vogel (Annalen, 44, 297), turmeric contains cellulose, gum, starch, mineral matter, a strong-smelling volatile oil, a brown colouring matter, and a characteristic yellow colouring matter named by them *Curcumin*. Pectin and pectic acid are also present (Schützenberger). Kachler (Ber., 3, 713) found a notable quantity of potassium binoxalate.

Pelletier and Vogel's method of isolating the curcumin consisted in first removing the fatty, resinous, and other impurities by extracting pulverised turmeric with water and carbon disulphide, then dissolving out the colouring matter with boiling alcohol, and purifying it by successive solution in ether and alcohol, precipitation with lead acetate, and subsequent treatment with hydrogen sulphide and ex-

traction of the product with ether. It was thus obtained as an amorphous yellow powder.

Lepage adopted a similar method, but after extraction with carbon disulphide the colouring matter was dissolved in alkali, precipitated with acid, and finally purified by means of ether.

Daube was the first to obtain curcumin in the crystalline state. He removed essential oil by passing a strong current of steam over the coarsely-ground turmeric, then thoroughly extracted it with hot water, and finally treated the dried residue with boiling benzene. On cooling the solution thus obtained, crude curcumin separated as bright orange-red crystalline crusts, which were pressed between blotting-paper, and dissolved in cold alcohol. After filtering off some yellow flocculent substance, the solution was precipitated with an alcoholic solution of neutral lead acetate, adding finally a little basic lead acetate in order to neutralise almost entirely the liberated acetic acid and prevent thereby any solution of the colour-lake. The brick-red precipitate was washed with alcohol, suspended in water, and decomposed with hydrogen sulphide. The liberated curcumin was extracted from the precipitate with boiling alcohol, from which it crystallised on slow evaporation.

Benzene is very suitable for the isolation of pure curcumin, for although it is very little soluble in this liquid, the resinous impurities are not dissolved thereby.

Gajewsky (Ber., 3, 265) obtained crystalline curcumin by first extracting turmeric root with carbon disulphide, then dissolving out the colouring matter with ether, and purifying it by fractional crystallisation from ether or benzene. He detected the presence of another colouring matter and also traces of an alkaloid. This chemist obtained an increased yield of colouring matter by washing the dry ethereal extract with dilute ammonia to remove resin, then dissolving the brittle residue in boiling concentrated ammonia solution and precipitating with carbon dioxide; 250 grms. ethereal extract gave 100 grms. flocculent curcumin, melting-point 140°. Jackson (Ber., 14, 485) also obtained crystallised curcumin by first removing the oil by long extraction with carbon disulphide (sixty hours), then thoroughly extracting (sixty hours) with ether, and after washing the orange-coloured product thus obtained with cold alcohol or ether, crystallising from hot alcohol.

Perkin (Chem. Soc. Trans., 1904, 85, 63) precipitates an alcoholic turmeric extract with lead acetate, washes the lead compound first with alcohol then with water, and decomposes it with dilute sulphuric acid. From the mixture of lead sulphate and curcumin the latter

is removed with boiling alcohol and the extract evaporated and poured into ether, which causes the separation of tarry impurities. The ethereal solution, after evaporation to a small bulk, is treated with carbon disulphide and allowed to stand, the crystals which separate from time to time being removed. 0·56 per cent. of curcumin was thus obtained from turmeric.

Curcumin crystallises from alcohol in orange-coloured prisms, melting-point 165° (Daube), 172° (Gajewsky), 178° (Jackson), and 183° (Ciamician and Silber, Ber., 30, 192), and is soluble in ether, forming a green fluorescent liquid. Alkaline solutions dissolve it with a reddish-brown colour, which when neutralised passes to yellow, and on this account it is useful in the form of "turmeric paper" as a reagent for alkalis. Whereas Daube assigned to curcumin the formula $C_{10}H_{10}O_3$, Gajewsky $(C_4H_4O)_n$, probably $C_{16}H_{16}O_4$, Jackson considered that $C_{14}H_{14}O_4$ or $C_{28}H_{28}O_8$ were more reasonable expressions, and of these Jackson and Menke (Amer. Chem. J., 6, 78) preferred the former, and prepared the following derivatives harmonising with this view:—

Dihydrocurcumin, $C_{14}H_{16}O_4$, brownish-white powder, melting-point 100° *ca.*; *dihydrocurcumin anhydride*, $C_{28}H_{30}O_7$, dirty white powder, melting-point 120° *ca.*; *diethylcurcumin*, $C_{18}H_{22}O_4$, brownish tar; *p-brombenzylcurcumin*, $C_{21}H_{19}BrO_4$, pale yellow crystals, melting-point 76—78°; *acetylcurcumin*, $C_{16}H_{16}O_5$, brownish mass; *diacetylcurcumin*, $C_{18}H_{18}O_6$, yellow rhombic crystals, melting-point 154°; *curcumintetrabromide*, $C_{14}H_{14}O_4Br_4$, powder, melting-point 185° *ca.*; *tetrabromcurcumin*, $C_{14}H_{10}Br_4O_4$, red powder; *pentabromcurcumindibromide*, $C_{14}H_9Br_5O_4 . Br_2$, red powder, melting-point 120° *ca.*; *potassium curcumin*, $KC_{14}H_{13}O_4$, red powder, and *dipotassium curcumin*, $K_2C_{14}H_{12}O_4$, red needles. By fusion with alkali curcumin gives *protocatechuic acid*, when oxidised with permanganate *vanillin*, and the diethyl ether by similar treatment yields *vanillic acid ethyl ether*. Jackson and Menke represented curcumin by the following formula:—

$$C_6H_3(OH)(OCH_3)CH(C_5H_5)CO_2H(CH:OCH_3:OH = 1:3:4)$$

More recently Heller (Ber., 1914, 47, 2998) has obtained *dihydrocurcumin*, now shown to possess the formula $C_{21}H_{24}O_6$, by catalytic reduction, as colourless needles, melting-point 95—96°.

Ciamician and Silber (Ber., 30, 192), as the result of methoxy determinations, assigned the formula $C_{21}H_{20}O_6$ or $C_{19}H_{14}O_4(OCH_3)_2$ to curcumin, and prepared *diacetylcurcumin*, $C_{21}H_{18}O_6(C_2H_3O)_2$, needles, melting-point 170—171°; and *curcumin dimethyl ether*, $C_{19}H_{12}O_2(OCH_3)_4$, yellow needles, melting-point 135°. Digested

with hydroxylamine hydrochloride in alcoholic solution curcumin gave the compound $C_{21}H_{19}NO_5$ (i.e. $C_{21}H_{20}O_5NOH—H_2O$), needles, melting-point 178°, whereas phenylhydrazine gave a substance crystallising in colourless needles.

Perkin (Chem. Soc. Trans., 1903, 83, 140, and 1905, 85, 63) by means of alcoholic potassium acetate, obtained from curcumin the monopotassium salt $C_{21}H_{19}O_6K$, fine orange-red needles. A *benzoyl curcumin*, pale yellow needles, melting-point 176—178°, was also prepared, and gave by the cryoscopic method numbers harmonising with Ciamician and Silber's formula.

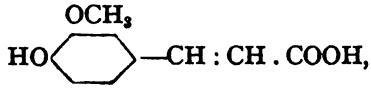
Molecular weight determinations, however, according to Jackson and Clarke (Ber., 1905, 38, 2712), indicated the correctness of the formula $C_{14}H_{14}O_4$, and again (*ibid.*, 1906, 39, 2269) these authors pointed out that unless special care is employed, Zeisel's method gives erroneous figures with curcumin. When heated with hydriodic acid at 120° a correct result is given, but above this temperature curcumin gives a colourless oil rich in iodine (75·75 per cent.) which reacts with the alcoholic silver nitrate solution.

v. Kostanecki and Lampe (*ibid.*, 1910, 43, 2163) consider that Ciamician and Silber's formula $C_{21}H_{20}O_6$ correctly represents curcumin, and describe *dicarbomethoxycurcumin*,

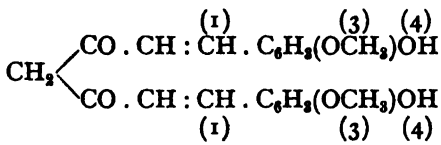
$$C_{19}H_{16}O_2(O \cdot COOCH_3)_2(OCH_3)_2,$$

yellow prisms, melting-point 150°, and *dicarbethoxycurcumin*, yellow leaflets, melting-point 149—150°.

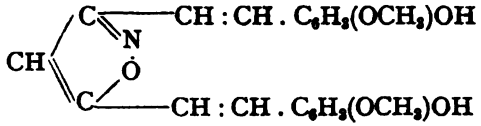
When curcumin is boiled with potassium hydroxide solution, *vanillic acid* and *ferulic acid*,



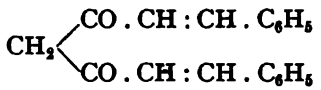
are produced. As a result these authors consider that the constitution of this colouring matter is as follows:—



Further support for this formula is given by the fact that curcumin, like β-diketones, gives when treated with hydroxylamine an *iso*-oxazole derivative, and the compound prepared by Ciamician and Silber is probably 4 . 4′-*dihydroxy* 3 . 3′-*dimethoxy*-a : 7 *distrylis-oxazole*—



Ryan and Dunlea (Proc. Roy. Irish Acad., 1913, 32, 9) attempted to obtain dicinnamoylmethane—

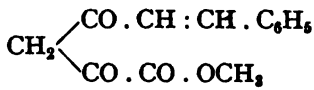


by condensing cinnamic ester with cinnamoyl acetone in the presence of sodium without success, though with saturated ketones such a reaction proceeds normally. Thus cinnamic ester and acetone give cinnamoyl acetone (cinnamoyl-acetyl-methane)—

$$C_6H_5 . CH : CH . CO . CH_2 . CO . CH_3,$$

a substance crystallising in yellow needles, melting-point 83—84°, and capable of dyeing mordanted wool.

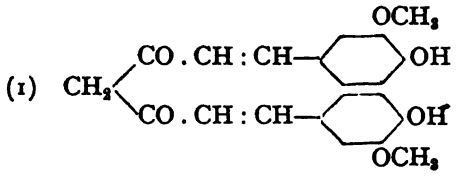
Ryan and Algar (*ibid.*, 1913, 32, 9) again obtained methylcinnamoyl pyruvate—

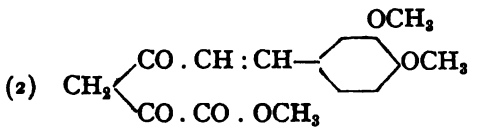


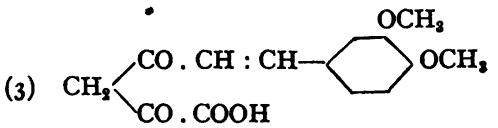
from cinnamyl methyl ketone and methyl oxalate which crystallises in yellow prisms, melting-point 70°, also capable of dyeing mordanted wool. Numerous compounds of this type have been described by Ryan and his co-workers, and in a paper by Ryan and Plumkett (*ibid.*, 1916, 199) a list of the dyeing properties of some of the compounds on wool is given, of which the following is an abstract:—

	Chromium.	Aluminium.	Tin.	Iron.
Cinnamoyl-acetyl-methane .	Dark yellow	Light yellow	—	Bright red
Cinnamoyl-benzoyl-methane	Dark yellow	Light yellow	—	Reddish-brown
Methyl cinnamoyl-pyruvate	Russet-brown	Orange-yellow	Light orange-yellow	Reddish-brown
Cinnamoyl-pyruvic acid .	Brown	Orange	Orange	Deep reddish-brown
p-methoxycinnamoyl-pyruvic acid	Chocolate-brown	Bright orange	Bright orange	Reddish-brown
3.4 dimethoxycinnamoyl-pyruvic acid . . .	Chocolate-red	Orange-red	Orange-brown	Dark chocolate-brown
Curcumin	Brown	Orange-yellow	Orange-red	Brown-black

The shades given by these compounds are of a similar nature to those produced by curcumin itself, and the results of these authors thus support v. Kostanecki's formula for this compound. In comparing the three compounds, curcumin (1), methyl 3 . 4 dimethoxy cinnamoyl-pyruvate (2), and 3 . 4 dimethoxycinnamoyl pyruvic acid (3),







Ryan and Plumkett point out that in all these compounds the same double chromophore —CO—CH : CH— is present, together with the acidic methylene radical which is here the auxochrome. Though in curcumin the double chromophore occurs twice, its effect is to some extent balanced by the fact that the methylene radical in $XCO . CH_2 . CO . COOR$ possesses much stronger auxochromic property than in the group $XCO . CH_2 . COX$. In curcumin, again, the auxochromic effect of the hydroxyls in the vanillin nuclei can only be slight.

In 1913 Lampe and Milobedzka (Ber., 46, 2233) succeeded in synthesising dicinnamoyl-methane, the mother substance of curcumin, in the following manner:—

Cinnamoylaceto-acetic ester (Fischer, Ber., 1883, 16, 166),

$$C_6H_5 . CH : CH . CO . CH(COOEt)COCH_3,$$

on hydrolysis and simultaneous loss of carbon dioxide gives cinnamoyl acetone—

$$C_6H_5 . CH : CH . CO . CH_2 . CO . CH_3$$

The monosodium derivative of this latter when condensed with cinnamic chloride gives dicinnamoyl-acetyl-methane (dicinnamoyl acetone)—

$$C_6H_5 . CH : CH . CO . CH(CO . CH_3) . CO . CH : CH . C_6H_5$$

which on hydrolysis splits off acetic acid with formation of dicinnamoyl-methane—

$$\begin{matrix} C_6H_5 . CH : CH . CO \\ C_6H_5 . CH : CH . CO \end{matrix} > CH_2$$

This compound, which crystallises in yellow prismatic needles, melting-point 144°, dissolves in sulphuric acid to form an orange-red solution possessing a yellow fluorescence. Both in its chemical and physical properties it closely resembles curcumin, and dyes cotton yellow shades which, however, are weaker than those given by curcumin itself.

In 1914 (Ber., 47, 887) Heller described a stereoisomeride of curcumin which he named *iso-curcumin*, and this he obtained as a reddish-yellow crystalline solid, sintering at 140° and melting near 180°, by condensing vanillin with acetylacetone in the presence of hydrochloric acid—

$$CH_2 < \begin{matrix} CO . CH_3 \\ CO . CH_3 \end{matrix} + 2C_6H_3(OH)(OCH_3) . COH =$$

$$CH_2 < \begin{matrix} CO . CH : CH . C_6H_5(OH)(OCH_3) \\ CO . CH : CH . C_6H_5(OH)(OCH_3) \end{matrix} + 2H_2O$$

Ryan and Dunlea (Proc. Roy. Irish Acad., 1915, 32, B., 657), however, criticised this statement. They find that the first product of the action of benzaldehyde on acetyl acetone in this way is not benzylidene acetone, $C_6H_5CH : CH . CO . CH_2 . CO . CH_3$, but a chlorinated compound which on heating *in vacuo* gives

$$CH_3—CO—\underset{\underset{\|}{CH}}{\underset{|}{C_6H_5}}—CO—CH_3$$

Iso-curcumin thus may be the trivanillin condensation product, with which indeed Heller's analytical results agree—

$$CH_3O(OH)C_6H_3 . CH : C < \begin{matrix} CO . CH : CH . C_6H_5(OCH_3)OH \\ CO . CH : CH . C_6H_5(OCH_3)OH \end{matrix}$$

Heller (Ber., 1914, 47, 2998), however, states that this criticism of Ryan and Dunlea is unjustified in that iso-curcumin is a chlorine

free colouring matter. Iso-curcumin shows a faint reaction with ferric chloride, and is to be regarded as a mixture of ketone with a little enol, whereas curcumin is decidedly enolic. *Ethylcarbanato-iso-curcumin* melts at 142°.

It is well known that a mixture of boric and hydrochloric acids imparts to turmeric paper a brown colour which is turned blue by alkalis. This reaction was investigated by Schlumberger (Bull. Soc. Chem., [ii.], 5, 194), who found that when an alcoholic extract of turmeric is heated in a sealed tube with boric acid, a red crystalline boric acid derivative is produced, soluble in alkaline solutions with a purple-violet colour. Boiling water decomposes this compound with elimination of boric acid, and formation of *pseudo-curcumin*, a yellow powder. If the alcoholic solution of the boric acid compound is digested with strong hydrochloric acid, a black substance separates, whereas boric acid remains in the liquid.

On extracting the black powder with a mixture of alcohol and acetic acid, the filtrate deposits green iridescent crystals of rosocyanine.

Rosocyanine is readily soluble in alcohol containing a trace of mineral acid and dissolves in ammonia solution with a blue colour. It is, according to Schlumberger, an unstable substance, and if boiled for a long time with alcohol, is converted into pseudo-curcumin.

Jackson and Clarke (*loc. cit.*) prepared rosocyanine by heating a solution of curcumin in dilute alcohol with boric and sulphuric acids, and describe it as a purplish-red powder, closely resembling powdered rosaniline. These authors considered it to be isomeric with curcumin, $C_{14}H_{14}O_4$, and described an *ammonium salt*, $C_{14}H_{13}O_4NH_4$, and a *potassium salt*, $C_{14}H_{13}O_4K$, both of which possess an intense blue colour.

The tinctorial properties of curcumin are of special interest, for not only is it a strong colouring matter towards mordants, but with cotton, wool, and silk it behaves also as a substantive dyestuff. In the latter case it is only necessary to add the material to a boiling decoction of the colouring matter. Though considerably employed up to within recent years by the wool and silk dyer in the formation of olives, browns, and other compound colours, turmeric is now but rarely used for dyeing purposes in England. In India, however, it appears to be still in vogue.

Cotton is usually dyed in a decoction of turmeric rendered slightly acid by the addition of a little acetic acid, or alum may be employed. The colour does not resist either the action of light or of alkalis, and readily acquires a brownish-red tint. Wool may be

dyed without any addition, keeping the temperature about 60°. By previously mordanting with alum a brighter effect is produced, whereas tin mordant gives a more orange colour. Potassium dichromate and ferrous sulphate employed in a similar manner yield respectively olive and brown coloured shades.

Silk is preferably dyed in an acid bath, and is sometimes previously mordanted.

Turmeric oil is the thick orange-coloured aromatic oil present to the extent of 3·23 per cent. in turmeric from which it can be extracted by means of carbon disulphide. Bolley examined the portion distilling over at 230—250°, and considered it to be identical with carvol, whereas Gajewsky (*loc. cit.*) found the portion distilling over at 220—228° contains less carbon and more hydrogen than that which passes over at a higher temperature. On oxidising the latter portion with chromic acid, an acid oil is obtained which contains valeric, caproic, and terephthalic acids. Jackson and Menke (*loc. cit.*) analysed that portion which distils over at 285—290°, and gave it the formula $C_{19}H_{28}O$, and the name *turmerol*, and obtained *turmeryl chloride*, $C_{19}H_{27}Cl$, *sodium turmerol*, $C_{19}H_{27}ONa$, and *turmerol* isobutyl *ether*, $C_{19}H_{27}O \cdot C_4H_9$. With permanganate turmerol gave *terephthalic acid*, *turmeric acid*, $C_{11}H_{14}O_3$, and *apoturmeric acid*, $C_{10}H_{12}O_4$ or $C_{10}H_{10}O_4$. According to Rüpe (Ber., 1907, 40, 4909), when turmeric oil is boiled with dilute sodium hydroxide solution a substance, boiling-point 156°/12 mm., apparently not identical with Jackson and Menke's turmerol, is produced. Stronger alkali yields an optically active ketone, $C_{13}H_{18}O$, *curcumone*, boiling-point 119—120°/8 mm., which gives a semicarbazone, melting-point 119·5—120·5°, an oxime, boiling-point 159°/11 mm., and condensation products with aromatic aldehydes. With permanganate the ketone gives p-*methylacetophenone* and *terephthalic acid*, and with alkaline hypobromite the acids $C_{12}H_{16}O_3$, melting-point 150°, and $C_{12}H_{16}O_2$, melting-point 33—34°. By the further action of permanganate the latter yields a dicarboxylic acid, $C_{12}H_{14}O_4$, melting-point 228°. Rüpe, Luksch, and Steinbach (Ber., 1909, 42, 1515) were unable to isolate from turmeric oil the turmerol of Jackson and Menke, having sp. gr. 0·9388 at 20° and $[\alpha]_D^{20} - 27·46$. By digestion with alcohol and 30 per cent. potassium hydroxide solution the ketone $C_{13}H_{18}O$, *curcumone*, was obtained, which has boiling-point 121°/10 mm., sp. gr. 0·9566 at 20°, n_D 1·50526, $[\alpha]_D$ 80·55, and yields the p-*bromophenylhydrazone*, melting-point 71°. It condenses with benzaldehyde to form the compound

$$C_{13}H_{16}O : CH \cdot C_6H_5,$$

melting-point 106°, and with piperonal and anisic aldehyde similar compounds melting respectively at 86° and 77—78° are produced.

The acid $C_{12}H_{16}O_2$ (*loc. cit.*), melting-point 33—34°, is called *curcumic acid*, and appears to be identical with Jackson and Menke's turmeric acid (Rüpe and Steinbach, Ber., 1910, 43, 3465). By oxidation with permanganate it gives terephthalic acid, *p*-tolymethylketone, and the acid $C_{12}H_{14}O_4$, melting-point 226—228° (*loc. cit.*), and this possibly consists of *apoturmeric acid* (Jackson and Menke). Although it was considered that curcumic acid might be γ-*p*-tolylvaleric acid, the synthesis of this latter compound showed that the two substances are similar but not identical (*ibid.*, 1911, 44, 584). Again, curcumic acid is not *p*-tolyl-α-methylbutyric acid (Rüpe and Bürgin, *ibid.*, 1218). Rüpe and Steinbach (*loc. cit.*) consider that curcumone is to be regarded as a benzene derivative containing two parasubstituents, one being methyl, and the second, one or other of the groups CHMe . CH_2 . CH_2COMe,

. CHMe . CHMe . COMe, or . CMeEt . COMe,

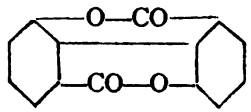
whereas in curcumic acid the group COMe is replaced by COOH. See also Schimmel & Co. (Ber., April, 1911).

CHAPTER XII.

DIPHENYL DIMETHYLOLID GROUP.

Introduction—Ellagic Acid—Flavellagic Acid—Coeruleoellagic Acid—Flavogallol—Resoflavine—Catellagic Acid—Metellagic Acid.

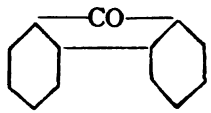
Diphenyl-dimethylolid—



the dilactone of dihydroxy-diphenyl dicarboxylic acid, is the mother substance of a small series of colouring matters, of which but one natural representative, ellagic acid, is as yet known to exist. The methylolid grouping —CO—O— present in the compounds has a feebler chromophoric character than the carbonyl itself, and on this account the dyeing properties of the members of this class are inferior as regards strength to those of the benzophenone, flavone, and allied dyestuffs. That the diphenyl linkage here exerts an influence is certain, for gallotannin containing as it does digalloyl nuclei—

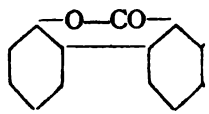
$$(OH)_3C_6H_2—CO—O—C_6H_2(OH)_2—CO—O—$$

dyes only with iron and titanium mordants, and again such an effect is clearly seen by a comparison of benzophenone and fluorenone—



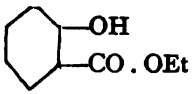
for whereas the former is colourless, the latter possesses a strong yellow tint.

Though diphenyl-dimethylolid is at present unknown, diphenyl methylolid—



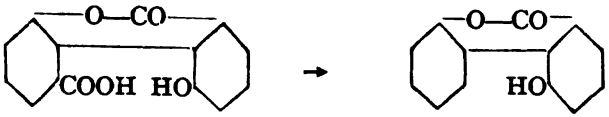
needles, melting at 92·5, has been prepared by various methods, and

of these that of Richter (J. pr. Chem., [2], 28, 294), who obtained it by the action of phosphorus oxychloride on ethyl salicylate—

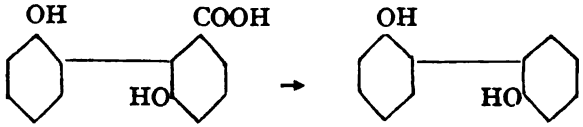


is the simplest.

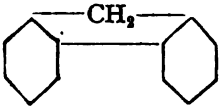
Colouring matters derived from diphenylmethylolid itself do not appear to exist in nature, though certain of them can be readily prepared by the action of alkali on dimethylolid compounds, in which case hydrolysis followed by the elimination of a carboxyl group occurs—



By a more drastic action of the alkali, hydroxydiphenyl derivatives are produced—



Interesting is the fact pointed out by Graebe (*loc. cit.*) that by distillation with zinc-dust diphenylmethylolid yields fluorene—



in addition to diphenyl and methyldiphenyl. Formerly the production of the first-named hydrocarbon from ellagic acid proved a stumbling-block in the attempts to obtain a clear conception of its constitution.

Ellagic Acid.

Ellagic acid, $C_{14}H_6O_8$, is obtained from numerous tannin matters which contain an ellagitannin by boiling the aqueous extract with dilute sulphuric acid. In many cases it is found in the free state, due probably to the hydrolysis, by fermentation, of the ellagitannin or ellagic acid glucoside originally present, and such a fermentation frequently occurs when aqueous extracts of the tannin matters are allowed to stand for some time.

Divi-divi (*Caesalpinia coriaria*, Willd.), (Löwe, Zeitsch. anal. Chem., 1876, 14, 40), myrobalans (*Terminalia chebula*, Ratz.),

(Löwe, *ibid.*), algarobilla (*Caesalpinia brevifolia*), (Zölffel, Beilstein, 2, 1085), and valonia (*Quercus aegilops*, Linn.) yield considerable quantities of ellagic acid, and are the best natural sources of this material. It has also been isolated from oak galls (Chevreul, Ann. Chim. Phys., 1828, (2), 9, 329); oak bark (Etti, Monatsh., 1880, 1, 226); the bark of *Picea excelsa* (Link.), (Strohmer, *ibid.*, 1881, 2, 539); pomegranate rind (Rembold, Annalen, 1867, 143, 288); *Quebracho colorado* (Perkin and Gunnel, Chem. Soc. Trans., 1896, 69, 1307); *Arctostaphylos uva-ursi* (Spreng.) and *Coriaria myrtifolia* (Linn.), (Perkin, *ibid.*, 1900, 77, 424); *Hæmatoxylon campeachianum* (Linn.), (Perkin, *ibid.*, 1897, 71, 1137); the fruit of *Caesalpinia digyna* (Rottl.), (Nierenstein, Chem. Zeit., 1909, 87); and the bark of *Terminalia catappa* (Linn.), (*ibid.*). In fact, ellagic acid probably always occurs, if only in minute quantity, in all plant products which contain gallotannin. Most interesting are the Oriental bezoar stones, concretions which are found in the stomachs of goats and other animals, and consist largely of ellagic acid. These originate, without doubt, from the fact that the animal has fed upon plants in which some quantity of an ellagitannin is present.

Ellagic acid was first discovered by Chevreul (Ann. Chim. Phys., *loc. cit.*) in oak galls, and more closely examined by Braconnot (*ibid.*, 9, 187). According to Pélouze, it possessed the composition $C_7H_4O_4$ (*ibid.*, 54, 356); whereas Merklein and Wöhler (Ann. Chem. Pharm., 55, 129), who isolated it from bezoar stones and termed it "bezoaric acid," showed that its true formula is $C_{14}H_6O_8$.

The precipitate of crude ellagic acid, which is produced by boiling the tannin extract with dilute mineral acid, is purified by washing with alcohol and subsequent recrystallisation. A similar procedure is also satisfactory with the deposits so frequently produced by fermentation and alluded to above. Ellagic acid is most readily crystallised from pyridine (Perkin and Nierenstein, Chem. Soc. Trans., 87, 1416), and the product, which contains pyridine of crystallisation, is washed with alcohol.

Löwe (Zeitsch. Chem., 1868, 4, 653) was the first to prepare ellagic acid synthetically by oxidising gallic acid with arsenic acid, and this was subsequently accomplished by Ernst and Zwenger (Annalen, 1871, 159, 32) by heating ethyl gallate with sodium carbonate solution in the presence of air, and by Griessmayer (*ibid.*, 1871, 160, 55) by heating gallic acid with water and iodine. It is readily produced by oxidising gallic acid dissolved in acetic acid by means of potassium persulphate and sulphuric acid (Perkin and Nierenstein, *loc. cit.*), and together with flavellagic acid by the addi-

tion of potassium persulphate to a solution of gallic acid in sulphuric acid (Perkin, *ibid.*, 1906, 89, 251). Under similar conditions, gallotannin produces ellagic acid (Nierenstein, Ber., 1908, 41, 3015; and 1909, 42, 353), and it can also be prepared by boiling the tannin with hydrogen peroxide solution (*ibid.*, 1907, 40, 917). Herzig and Bronneck obtained good results by passing air through an ammoniacal solution of gallic acid, and also of gallotannin (Montash., 1908, 29); whereas Sisley (Bull. Soc. chim., 1909, [4], 5, 727) prepared ellagic acid from tannin by means of alcoholic potassium hydroxide solution. According to Rüpe, a 60 per cent. yield is produced when gallic acid in sulphuric acid solution is oxidised with sodium nitrite (Chemie d. naturl. Farbstoffe, 1909, 2, 162).

Ellagic acid crystallised from pyridine forms prismatic needles, which are converted by alcohol into a pale yellow crystalline powder; but when purified by means of its acetyl derivative, the product is almost colourless (Perkin and Nierenstein). It is very sparingly soluble in all the usual solvents, dissolves in alkaline solutions with a pale yellow colour, and from these liquids, when diluted with hot alcohol, is deposited on acidifying in a crystalline condition. When heated it does not melt below 360°; and sublimes at higher temperatures with considerable carbonisation. With nitric acid containing nitrous acid and subsequent dilution, it gives a blood-red coloration (Griessmayer's reaction), and this reaction, considered to be characteristic, is known to be also possessed by flavellagic acid (Perkin).

According to Merklein and Wöhler (*loc. cit.*), the alkaline solution of ellagic acid becomes reddish-yellow on exposure to air, and deposits black crystals of potassium glaucomelanate, $K_2C_{12}H_{14}O_7$. When boiled with phenylhydrazine in alcoholic solution, or when carefully heated with phenylhydrazine, ellagic acid forms the product $C_6H_5NH.NH_2$, $C_{14}H_6O_8$, which crystallises in yellow needles, and is readily reconverted into ellagic acid. Ellagic acid gives similar compounds with aniline and quinoline (Goldschmiedt, Monatsh., 1905, 26, 1139).

Tetraacetylellagic acid, $C_{14}H_2O_8(C_2H_3O)_4$, (Barth and Goldschmiedt, Ber., 1878, 11, 846; Schiff, *ibid.*, 1879, 12, 1534; Zölffel, Arch. Pharm., 229, 123), colourless needles, melting-point 343—346° (Perkin and Nierenstein); *tetrabenzoylellagic acid*, $C_{14}H_2O_8(C_7H_5O)_4$, colourless needles (Goldschmiedt and Jahoda, Monatsh., 1892, 13, 151), melting-point 332—333° (Perkin); *ellagic acid monomethyl ether*, $C_{14}H_5O_7(OCH_3)$, yellow crystalline powder (Goldschmiedt, Monatsh., 1905, 26, 1139); *diacetylellagic acid monomethyl ether*,

$C_{14}H_3O_7(OCH_3)(C_2H_5O)_2$, crystalline powder (Goldschmiedt); *ellagic acid dimethyl ether*, $C_{14}H_4O_6(OCH_3)_2$, crystalline powder (Goldschmiedt); and *ellagic acid tetramethyl ether*, $C_{14}H_2O_4(OCH_3)_4$, colourless microscopic needles (Goldschmiedt; Herzig and Pollak, Monatsh., 1908, 29, 263), have been described.

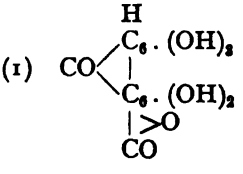
Ellagic acid gives the following salts: $KC_{14}H_5O_8$, minute yellow needles (Perkin and Wilson, Chem. Soc. Trans., 1903, 83, 134); $K_2C_{14}H_4O_8$, prisms (Merklein and Wöhler; Perkin and Wilson); $K_2C_{14}H_4O_8$, KOH, microscopic prisms (Merklein and Wöhler); $Na_2C_{14}H_4O_8$, crystalline powder; $NaC_{14}H_5O_8$, H_2O, yellow needles (Ernst and Zwenger, Annalen, 1871, 159, 32).

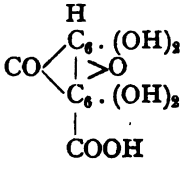
The tinctorial properties of ellagic acid are somewhat feeble, but in 1887 it was placed on the market by Messrs. Meister, Lucius, & Brüning, under the name of "Alizarin Yellow in paste," and was recommended as yielding, with chromium mordants, greenish-yellow shades of considerable permanence.

Rembold (Annalen, 1867, 143, 288) states that when ellagic acid is treated with sodium amalgam, it gives *γ-hexahydroxydiphenyl*, $C_{12}H_4(OH)_6$, three distinct *rufohydroellagic acids*, $C_{14}H_{10}O_6$, $C_{14}H_{10}O_7$, $C_{14}H_{10}O_9$, and *glaucohydroellagic acid*; but, according to Nierenstein (Ber., 1908, 41, 1649), this latter compound is in reality the pentahydroxydiphenylmethylolid referred to later. By the action of boiling potassium hydroxide solution (Barth and Goldschmiedt, Ber., 1879, 12, 1242), ellagic acid gives *hexahydroxydiphenyleneketone* (?) $C_{12}H_8O_7$, by fusion with potassium hydroxide *β-hexahydroxydiphenyl*, and by fusion with sodium hydroxide *γ-hexahydroxydiphenyl*, together with some of the *β*-compound.

When ellagic acid is distilled with zinc-dust *fluorene* is produced (Rembold, Ber., 8, 1494; Barth and Goldschmiedt, *ibid.*, 11, 846; cf. also Graebe, *ibid.*, 1903, 36, 212).

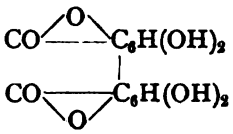
As a result of their investigation, Barth and Goldschmiedt (*ibid.*, 1879, 12, 153) suggested that ellagic acid could be represented by one of the two following formulæ:—

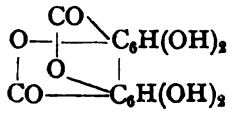
(1)


(2)


and of these the first was preferable.

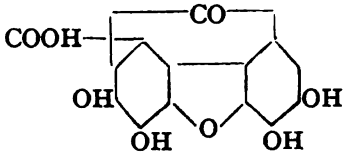
Whereas such a constitution requires the presence of five hydroxyl groups, Schiff (Ber., 1879, 12, 1534) considered that acetylellagic acid was $C_{14}H_2(C_2H_3O)_4O_8$, and this was subsequently corroborated by Zölffel (Arch. Pharm., 229, 123). Schiff, at the same time, proposed two formulæ for ellagic acid:—

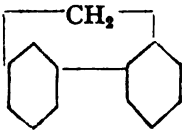
(1) 

(2) 

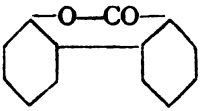
the latter of which is identical with that preferred by Graebe (*loc. cit.*). In a later investigation, Goldschmiedt and Jahoda (Monatsh., 13, 49), as the result of their preparation of tetrabenzoylellagic acid, were satisfied of the existence in ellagic acid of but four hydroxyls, and consequently adopted their second formula.

Graebe (Ber., 1903, 36, 214), among other criticisms, pointed out that a substance having this constitution, and which may be more clearly written as follows (1):—

(1) 

(2) 

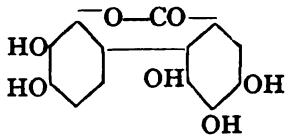
would yield, on distillation with zinc-dust, not fluorene, but an isomeric hydrocarbon (2), if this, indeed, were capable of existence. In the same paper this author announced the interesting fact that diphenylmethylolid—



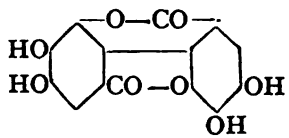
on distillation with zinc-dust, gives not only diphenyl and methyldiphenyl, but also *fluorene*; and in a theoretical discussion of the subject, suggested that Schiff's second formula (given above) most probably represents the true constitution of this substance.

The subject was reinvestigated somewhat later by Perkin and Nierenstein (*loc. cit.*), who, on digesting ellagic acid with boiling potassium hydroxide solution, obtained Barth and Goldschmiedt's so-called hexahydroxydiphenyleneketone, $C_{12}H_8O_7$. From this

substance a *pentaacetyl* derivative, $C_{12}H_2O_7(C_2H_3O)_5$, prismatic needles, melting-point 224—226°, and a pentabenzoyl derivative, $C_{12}H_2O_7(C_7H_5O)_5$, plates, melting-point 257—259°, were prepared. As, moreover, zinc-dust distillation gave fluorene, there could be little doubt that this compound was in reality *pentahydroxydiphenylmethylolid*, as, indeed, was surmised by Graebe—



From their results, together with a study of other similar compounds, Perkin and Nierenstein considered that Schiff's formula, also advocated by Graebe, and which can be more clearly written thus—

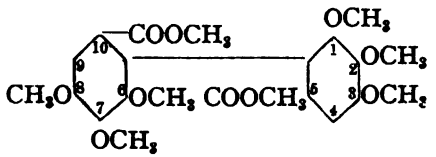


is a correct representation of the constitution of ellagic acid.

Finally, Herzig and Pollak (Monatsh., 1908, 29, 263), by a study of the methylation products of ellagic acid, obtained results further corroborating this constitution.

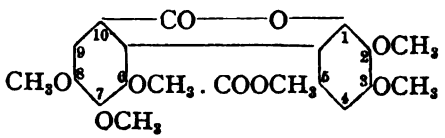
When Goldschmiedt's tetramethylellagic acid is digested with alcoholic potash and methyl iodide *diphenyl*-1 : 2 : 3 : 6 : 7 : 8-*hexamethoxy*-5 : 10-*dicarboxylic methyl ester* (melting-point 109—111°)—

(1)



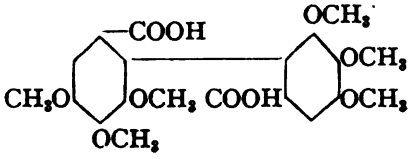
is obtained, together with a small quantity of *diphenylmethylolid*-2 : 3 : 6 : 7 : 8-*pentamethoxy*-5-*carboxylic acid methyl ester* (2), melting-point 187—189°—

(2)

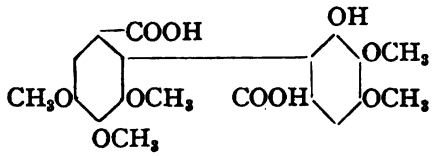


By means of alcoholic potash, these compounds (1) and (2) yield respectively *diphenyl*-1 : 2 : 3 : 6 : 7 : 8-*hexamethoxy*-5 : 10-*dicarboxylic acid* (3), melting-point 238—240°, and *diphenyl*-2 : 3 : 6 : 7 : 8-*pentamethoxy*-1-*hydroxy*-5 : 10-*dicarboxylic acid* (4), melting-point 200—203°—

(3)



(4)



Ellagic acid is probably not a tanning material in the true sense of the term, but is of considerable importance nevertheless in the tanning process. Thus the ellagitannic acid absorbed by the hide is at least in part converted into ellagic acid, and the deposit thus formed adds weight and bloom to the finished article.

Other members of this group have been prepared from *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, proto-catechuic acid, sym. dihydroxybenzoic acid, gallic acid, and from ellagic acid itself. An account of these is given below.

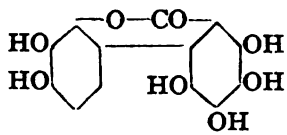
Flavellagic Acid.

Flavellagic acid, $C_{14}H_6O_9$, is obtained in conjunction with ellagic acid when gallic acid is oxidised with potassium persulphate and strong sulphuric acid. By the employment of a dilute acid, flavellagic acid almost free from ellagic acid can be produced, and for this purpose the following process is recommended (A. G. Perkin, Chem. Soc. Trans., 1906, 89, 251): 20 grams of gallic acid are treated with 160 c.c. of 96 per cent. sulphuric acid, 66 c.c. of water added, and the hot solution thus obtained is cooled to 50°, and maintained at this temperature during the gradual addition of 40 grams of potassium persulphate. A. G. Perkin and F. M. Perkin (Chem. Soc. Trans., 1908, 93, 1194) have obtained the same compound by the electrolytic oxidation of gallic acid in the presence of sulphuric acid, and more recently Bleuler and Perkin (*ibid.*, 1916, 109, 530) have prepared it by heating gallic acid at 110—120° with arsenic and sulphuric acids.

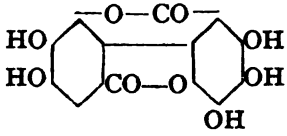
Flavellagic acid crystallises from pyridine in small yellow prismatic needles which contain pyridine, and do not melt below 360°. With nitric acid containing nitrous acid and subsequent dilution, it gives the blood-red coloration (Griessmayer reaction), which is also produced by ellagic acid. Dilute alkalis dissolve it with a yellowish-green coloration, and by distillation with zinc-dust *fluorene* is produced. *Acetylflavellagic acid*, $C_{14}HO_9(C_2H_3O)_5$, colourless needles, melts at 317—319°, and *benzoylflavellagic acid*, $C_{14}HO_9(C_7H_5O)_5$, prismatic needles, melts at 287—289°. Flavellagic acid dyes mordanted woollen cloth shades somewhat resembling but stronger than those produced by ellagic acid.

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Yellowish-olive.	Pale greenish-yellow.	Pale yellow.	Dark olive-brown.

By the action of boiling 50 per cent. potassium hydroxide solution, flavellagic acid gives *hexahydroxydiphenylmethylolid*—



colourless needles (melting-point above 300°). This compound dissolves in solutions of the alkali hydroxides with an orange-yellow tint, and this, on dilution with water and exposure to air, develops a strong bluish-violet coloration. The *acetyl* derivative, $C_{12}H_2O_8(C_2H_3O)_6$, colourless prismatic needles, melts at 232—234°. Flavellagic acid is hydroxyellagic acid, and possesses the following constitution :—

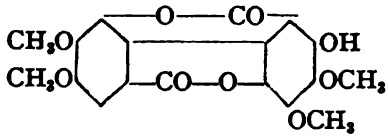


(cf. Herzig and Tscherne, Monatsh., 1908, 29, 281).

Flavellagic acid gives with diazomethane the *methyl ether* $C_{14}HO_4(OMe)_5$, melting-point 245°; and this is converted by methyl iodide and potassium hydroxide into *methyl*-3 : 4 : 5 : 6 : 2′ : 3′ : 4′-*heptamethoxydiphenyl*-2 : 6′-*dicarboxylate* $C_{12}H(OMe)_7(CO_2Me)_2$, melting-point 83—87°. The latter, on hydrolysis with potassium hydroxide, yields the *acid* $C_{12}H(OMe)_7(CO_2H)_2$, melting-point 163—167°, in the anhydrous condition. From water it crystallises with

$1H_2O$ and then melts at 95—100° (decomp.), (M. von Bronneck, Monatsh., 1908, 29, 281).

When gallic acid 3 : 4-dimethylether, or gallic acid trimethylether is oxidised by means of potassium persulphate and sulphuric acid at 45° (Herzig and Schmidinger, Monatsh., 1910, 31, 918), *flavellagic acid tetramethylether*—



yellow needles, melting-point 270—271°, is produced, the acetyl derivative of which melts at 270—271°. By means of methyl sulphate and potassium hydroxide, the heptamethoxy compound (described above) is obtained.

Coeruleoellagic Acid.

Coeruleoellagic acid is prepared by heating ellagic or flavellagic acids (1 part) with sulphuric acid (monohydrate 10 parts) to 200° and allowing the temperature to fall to 185—190° and remain there for thirty minutes. The product isolated by pouring into water is purified by conversion into its acetyl derivative, and this is subquently hydrolysed by means of sulphuric acid in the presence of acetic acid. It may also be obtained by the oxidation of ellagic or flavellagic acids (1 part) in sulphuric acid solution (10 parts) with arsenic acid (1 part) at 100—130° (Perkin, Chem. Soc. Trans., 1916, 109, 529).

Coeruleoellagic acid, $C_{14}H_6O_{10}$, separates from hot pyridine in small pale yellow prismatic needles which melt above 360° and are very sparingly soluble in the usual solvents. Concentrated solutions of the alkali hydroxides dissolve it with a greenish-yellow colour, which on dilution become green and finally of a blue colour, and these changes appear to arise from oxidation. Sodium and potassium carbonate solutions also give blue liquids. On distillation with zinc-dust fluorene is produced.

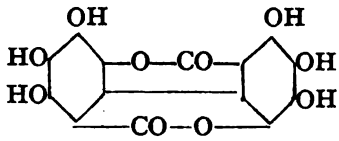
Acetylcoeruleoellagic acid, $C_{14}O_{10}(C_2H_3O)_6$, colourless needles, melting-point 330—332°, and *benzoylcoeruleoellagic acid*,

$$C_{14}O_{10}(C_7H_5O)_6,$$

melting-point 343—345°, have been prepared. The latter is more sparingly soluble in benzoic anhydride than the corresponding derivative of flavellagic acid, and this property provides a means for the separation of the two substances.

By digestion with 50 per cent. potassium hydroxide solution diluted with its own volume of alcohol, coeruleoellagic acid gives a compound $C_{12}H_{10}O_8$, evidently *octohydroxydiphenyl*. This consists of an almost colourless crystalline powder, soluble in dilute potassium hydroxide solution, with a reddish-violet coloration which becomes brown on exposure to air. The *acetyl* derivative, $C_{12}H_2O_8(C_2H_3O)_8$, forms colourless needles melting at 177—178°.

The constitution assigned to coeruleoellagic acid is as follows:—



a formula which represents it as either a dihydroxy-ellagic or hydroxy flavellagic acid.

Coeruleoellagic acid possesses well-marked dyeing properties of a similar character, though more strongly developed than those of ellagic and flavellagic acids, and may have practical utility. Owing to its sparing solubility it gives the best results in the paste form. The following results are obtained by the employment of mordanted woollen cloth:—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Deep olive-yellow.	Greenish-yellow.	Dull yellow.	Greenish-black.

In the case of the aluminium mordant the employment of chalk in the dye-bath exerts a detrimental effect.

FLAVOGALLOL.

When gallic acid in sulphuric acid solution is treated with arsenic acid and the mixture heated at 110—120° for six hours, a mixture containing flavellagic and coeruleoellagic acids is mainly produced, though when the oxidation is carried out in the presence of 80 per cent. sulphuric acid *flavogallol*, $C_{21}H_8O_{12}$, is obtained. This consists of hair-like yellow needles, sparingly soluble in the usual solvents, soluble in sodium hydroxide solution with an orange-yellow colour. With sulphuric acid it yields the *anhydrosulphate* $C_{21}H_6O_{11} . H_2SO_4$, orange-yellow prisms, whereas the *tripotassium* salt, $C_{21}H_5O_{12}K_3$, prepared with alcoholic potassium acetate forms an orange-coloured crystalline powder.

Acetylflavogallol, $C_{21}H_2O_{12}(C_2H_3O)_6$, small prismatic needles, melts and decomposes at 278—280°, and the corresponding *benzoyl*

compound, $C_{21}H_2O_{12}(C_7H_5O)_6$, yellow prisms, at 326—328°. With boiling aniline flavogallol yields the *anilide* $C_{21}H_7O_{11}.NH.C_6H_5$, which crystallises in yellow needles, melting above 345°. In the paste form flavogallol readily dyes mordanted fabrics, and employing woollen cloth the following shades are produced:—

Chromium.	*Copper.*	*Tin.*	*Iron.*
Dull olive-yellow.	Pale brown.	Pale orange-yellow.	Brownish-black.

When acetyl flavogallol is hydrolysed by the acetic ether method, *ethyl flavogallonate*, $C_{23}H_{14}O_{13}$, pale yellow needles, is produced, and in a similar manner by the employment of methyl alcohol in this process *methyl flavogallonate*, $C_{22}H_{12}O_{13}$, is obtained. By gentle treatment with strong potassium hydroxide solution flavogallol gives *flavogallonic acid*, $C_{21}H_{10}O_{13}$, needles, which melt above 300°, and this when acetylated is reconverted into acetyl flavogallol.

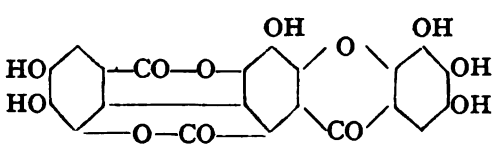
The more energetic action of potassium hydroxide solution gives *flavogallone*, $C_{20}H_{10}O_{11}$, minute needles, and this yields the acetyl compound $C_{34}H_{24}O_{18}$, leaflets, melting-point 257—259°.

When flavogallol is methylated with alkali and methyl sulphate and the product is digested with 5 per cent. potassium hydroxide, two apparently isomeric acids, $C_{21}H_4O_5(OMe)_{10}$, (*a*) colourless prisms, melting-point 206—208° and (*b*) melting-point 238—240°, are obtained, and these both appear to be produced by the addition of three molecules of water to flavogallol and a subsequent methylation of ten hydroxyl groups. These are dicarboxylic acids, and when esterified give the dimethyl ethers of the formula

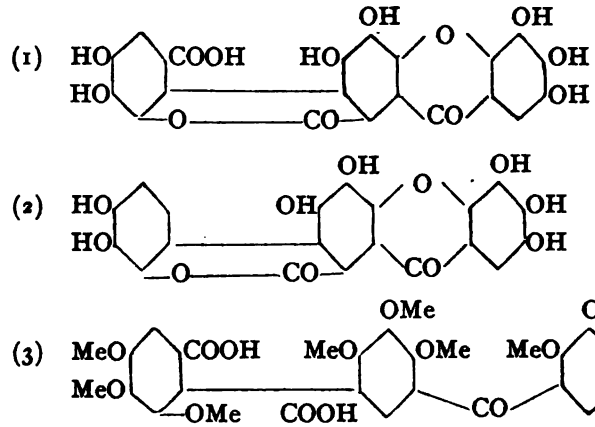
$$C_{29}H_{22}O_{11}(CO_2Me)_2,$$

(*a*) melting at 128—130°, and (*b*) at 86—87°.

The acid, melting-point 206—208°, when digested with alcoholic potash at 175° loses one methoxy group with formation of a new acid, $C_{28}H_{20}O_{11}(CO_2H)_2$, which crystallises in glistening leaflets, melting-point 183—184°. These reactions suggest the presence in flavogallol of an ellagic acid nucleus, and as a result Bleuler and Perkin (Chem. Soc. Trans., 1916, 109, 543) have tentatively suggested the formula—



for this colouring matter. In case this should prove correct flavogallonic acid (1), flavogallone (2), and the dicarboxylic acid obtained by methylation, melting-point 206—208° (3), will possess the following constitutions:—



Resoflavine.

This yellow dyestuff, $C_{14}H_6O_7$, obtained by the action of potassium persulphate and sulphuric acid on 3 : 5 dihydroxybenzoic acid was first examined by Herzig and Tscherne (Monatsh., 1904, 25, 603). This yields the *acetyl* derivative $C_{14}H_3O_7(C_2H_3O)_3$, and when methylated by means of diazomethane the yellow *trimethyl ether* $C_{14}H_6O_4(OMe)_3$, melting-point 286—288°.

When heated with methylic iodide and alcoholic potassium hydroxide, resoflavine trimethyl ether is converted into the ester

$$COOMe \cdot C_{12}H_3(OMe)_5 \cdot COOMe,$$

melting-point 132—134° (Annalen, 1907, 351, 24); this on hydrolysis gives first the ether acid, melting-point 197—199°,

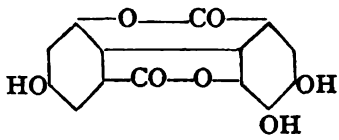
$$COOH \cdot C_{12}H_3(OMe)_5 \cdot COOMe,$$

and subsequently the dicarboxylic acid

$$COOH \cdot C_{12}H_3(OMe)_5 \cdot COOH,$$

which melts at 247—249°.

By fusion with alkali (Herzig and Epstein, *ibid.*, 661) resoflavine gives 3·5 dihydroxybenzoic acid, whereas on distillation with zinc-dust fluorene is produced. Resoflavine (Herzig and Tscherne, *ibid.*, 1908, 29, 281) is evidently a trihydroxydiphenyldimethylolid—

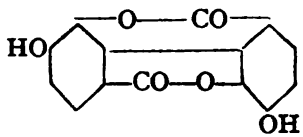


closely related to ellagic acid, which is in fact to be regarded as its monohydroxy derivative.

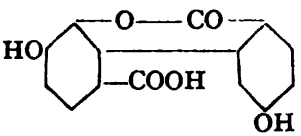
Catellagic Acid.

Schiff (Ber., 12, 2590) on heating protocatechuic acid with arsenic acid, obtained a substance which he named *catellagic acid*, and to this he assigned the formula $C_{14}H_{10}O_7$ or $C_{14}H_8O_7$. Perkin and Nierenstein (Chem. Soc. Trans., 1905, 87, 1417) obtained a similar substance by the oxidation of protocatechuic acid, and also parahydroxybenzoic acid with potassium persulphate and sulphuric acid. According to the latter authors, catellagic acid, $C_{14}H_6O_6$, crystallises from pyridine in colourless needles, which melt above 360°, and sublime with but moderate carbonisation at higher temperatures. Solutions of the alkali hydroxides dissolve it with a pale yellow colour, and with nitric acid it gives a magenta coloured liquid. *Diacetylcatellagic acid*, colourless prismatic needles, melts at 322—324°.

Catellagic acid, by distillation with zinc-dust, gives *fluorene*, and is closely related to ellagic acid. Its constitution (Perkin and Nierenstein) may be expressed as follows:—



From the oxidation products of parahydroxybenzoic acid, Perkin and Nierenstein isolated, in addition to catellagic acid, a second compound $C_{14}H_8O_6$, colourless needles, melting-point above 360°. This, which gives the diacetyl derivative $C_{14}H_6O_6(C_2H_3O)_2$, colourless needles, melting-point 267—268°, and by distillation with zinc-dust fluorene, possesses the formula—



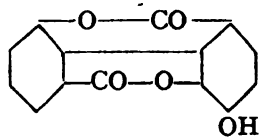
and evidently originates from the interaction of one molecule of protocatechuic acid and one of parahydroxybenzoic acid.

Metellagic Acid.

Metellagic acid (Perkin and Nierenstein, Chem. Soc. Trans., 1905, 87, 1425) is obtained in small amount together with other substances by oxidising metahydroxybenzoic acid in sulphuric acid solution with potassium persulphate at about 30°. The product is fractionally crystallised from acetic acid, the second crop acetylated, the acetyl derivative thus obtained purified by repeated crystallisation from acetic anhydride and hydrolysed with sulphuric acid in the usual manner.

Metellagic acid, $C_{14}H_6O_5$, crystallises from acetic acid in colourless needles which readily sublime at high temperatures. With caustic alkaline solutions it behaves similarly to catellagic acid giving a yellow colour which is discharged on heating. Distilled with zinc-dust a small quantity of a crystalline hydrocarbon is produced which appears to be identical with fluorene. *Acetylmetellagic acid*, $C_{14}H_5O_5(C_2H_3O)$, crystallises in colourless leaflets, melting-point 269—271°.

The reactions of metellagic acid are in harmony with those required by a member of the ellagic acid series, and the following formula assigned to it is probably correct.:—



In the mother liquors obtained during the purification of acetyl metellagic acid, a second acetyl compound, melting-point 237—243°, was isolated. This on hydrolysis gave a substance crystallising in glistening yellow needles, the nature of which has not been ascertained.

By the oxidation of suitable hydroxybenzoic acids, a series of hydroxydiphenyldimethylolid derivatives have thus been prepared, viz. :—

Metellagic acid, $C_{15}H_5O_4(OH)$	Ellagic acid, $C_{14}H_2O_4(OH)_4$
Catellagic acid, $C_{15}H_4O_4(OH)_2$	Flavellagic acid, $C_{14}HO_4(OH)_5$
Resoflavine, $C_{14}H_3O_4(OH)_3$	Coeruleoellagic acid, $C_{14}O_4(OH)_6$

CHAPTER XIII.

THE TANNINS.

Gall-nuts—Chestnut Extract—Sumach—Myrobalans—Valonia—Divi-divi—Algarobilla—*Quebracho colorado*.

Tannins.

Tannins (*Acides tanniques*, Fr.; *Gerbstoffe*, Ger.). — This term has been applied to a large class of substances which have been found in many plants and are distinguished by the following characters: they have an astringent taste; give a blue-black or green coloration with ferric salts; are precipitated by a solution of gelatin, by albumen and by alkaloids; unite with hide to form leather.

It was formerly believed that only one tannin existed, and it was assumed that the difference in properties of tannin from different sources was due to the presence of foreign matter. It is, however, now well known that tannin from different sources frequently varies both in composition and in properties, and although it is probable, owing to the difficulty of obtaining these compounds in an even approximately pure condition, that the number of distinct individuals may not be so great as is usually supposed, there can be no doubt that at least three important classes of tannins exist in nature. The earliest suggestion was to divide the tannins into two classes—the iron-blueing tannins and the iron-greening tannins—according to their behaviour towards salts of iron, and it was considered that whereas the former were pyrogallol compounds, that the latter were derived from catechol. This differentiation appears in the main to be correct, and the employment of ferric chloride for this purpose, or better, iron alum as a preliminary step, is of general application; but on the other hand, it is to be borne in mind that the presence of acid, alkali, or organic impurity has considerable effect upon the colour production. Thus, although the method is no doubt of service in many cases even with the plant infusion, its exact significance can only be ascertained from the coloration given by the purified tannin itself.

Stenhouse (Proc. Roy. Soc., 11, 405) believed that those tannins which give blue-black precipitates with ferric salts are mostly glucosides. Wagner (Zeitsch. anal. Chem.) made a distinction between *pathological* and *physiological* tannins, and considered that the former class represented by gallotannic acid only existed in pathological formations of certain species of oak and sumach (*Rhus javanica*, Linn., and *R. semilata*, Murr.), whilst the latter class include all tannins which are produced under normal conditions of plant life. As, however, gallotannic acid has been found to exist in some plants as a physiological tannin, Wagner's classification is untenable.

Böttinger (Ber., 1884, 17, 1123) has examined the action of bromine on aqueous tannin extracts, and determined the percentage of bromine contained in the precipitated bromo products. As a result, it was shown that certain tannins may be grouped together according to the amount of bromine which they take up.

Mangrove tannin	42·15
Hemlock bark tannin	43·6
Quebracho tannin	44·5
Mimosa tannin	49·36
Chestnut oak tannin	50·48
Terra japonica tannin	53·2
Spruce bark tannin	52·8

A very large amount of attention has been given to the classification or identification of aqueous extracts of tanning materials, by the coloured and other effects given by certain reagents. It remains to be decided whether in all cases these reactions in reality arise from the tannin itself.

The more important methods which may be used to classify the tannins into groups according to our present knowledge of these substances are as follows:—

Coloration with ferric chloride or iron alum (see above).

Digestion with boiling dilute sulphuric acid.—In this method of procedure, three definite reactions may be observed: (*a*) the hydrolysis of the tannin with formation of gallic acid (gallotannic acid); (*b*) the precipitation of ellagic acid (ellagitannic acid); (*c*) the gradual production of an amorphous red-coloured precipitate known as a "phlobaphene" (catechol or phlobatannin).

Precipitation with bromine water indicates the presence of a so-called catechol or phlobatannin (Procter, "Leather Industries Handbook," 1898).

Pine wood and hydrochloric acid test.—If a deal shaving be moistened with a solution of phloroglucinol and then with strong hydrochloric acid, a deep red-violet colour due to the formation of phloroglucinol vanillein is produced. Resorcinol reacts similarly giving a blue-violet (Procter). These colorations are an indication of the presence of a phloroglucinol or resorcinol nucleus in the tannins. Gallotannin and ellagitannin solutions do not react in this manner.

Diazobenzene chloride.—Solutions of certain tannins in the presence of alkali or alkaline acetates give a red-coloured precipitate of the azobenzene tannin with this reagent, a fact which indicates with some certainty the presence of a phloroglucinol or resorcinol grouping. Gallotannin and ellagitannin do not react in this manner.

Fusion with alkali.—Procter ("Leather Industries Handbook," 1898) recommends adding 20 grams of tannin to 150 c.c. of a solution of potassium hydroxide of specific gravity 1·20 and concentrating the liquid during three hours until it becomes pasty. Or 5 to 10 parts of caustic potash and a few drops of water are heated with one part of the tannin to 210—240° for twenty minutes. Gallotannin, by this method, gives gallic acid, and possibly traces of pyrogallol, whereas the so-called catechol tannins yield protocatechuic acid or other allied acid, alone, or together with phloroglucinol or resorcinol, etc.

Heating with glycerol.—The tannin (1 gram) is heated with 5 c.c. of glycerol slowly raising the temperature from 160°, and keeping it for half an hour between 200—210°. The product diluted with 20 c.c. of water is extracted with ether, the extract evaporated and the residue tested for pyrogallol or catechol. According to Trimble ("The Tannins"), paraffin wax may be employed in place of glycerol.

Formaldehyde test.—When an aqueous solution of a so-called catechol tannin is treated with formaldehyde and a little hydrochloric acid and gently warmed the tannin is completely precipitated. Pyrogallol tannins do not yield an entirely insoluble compound in this manner. This reaction, discovered by Stiansy (Der Gerber, 1905, 185), has by numerous writers been assigned to Jean and Frabot (Ann. Chim. anal., 1907, 12, 49).

Lead acetate test.—(Stiasny and Wilkinson, Collegium, 1911, 475 (2 ix.), 318). All natural tannins are completely precipitated by lead acetate solution in so far as the filtrate from the precipitate does not give the iron test. In the case of catechol or phlobatannins this precipitate is dissolved by dilute acetic acid, whereas with the

gallotannins the lead compound is insoluble or but partially soluble. The test is preferably made by adding 10 c.c. of acetic acid (10 per cent.) to 5 c.c. of the tannin solution, and then adding 5 c.c. of lead acetate (10 per cent.). No precipitate is thus produced in the case of the catechol or phlobatannins.

By these methods it is easy to divide the tannins into three classes, usually distinguished as (1) gallotannins, (2) ellagitannins, and (3) catecholtannins. Since the discovery of synthetical tannins by Fischer and Freudenberg (Annalen, 1911, 384, 225), it is evident that this nomenclature, as applied to the first group, is imperfect. Thus, whereas the term "gallotannin" is in reality only applicable to compounds containing pyrogallol nuclei and in fact merely relates to digallic acid and its derivatives, it is now known that diprotocatechuic acid, diresorcylic acid, and digentisic acid, members of the same group, possess tanning property. On this account it is considered more reasonable to distinguish such tannins by the term "depside," a nomenclature which is due to Fischer and Freudenberg, although it is not suggested that such a group is absent in the other tannins.

Again, as regards the so-called "ellagitannin" group (2), new tannins belonging to this class may also be either synthesised or isolated in the future. The term "ellagitannin" is therefore here replaced by "diphenyldimethylolid," the name by which the group mother substance is known.

Exception is again to be taken to the designation "catechol" tannin (3) for reasons similar to those given above and which are discussed later in this article, and this name is also replaced by "phlobatannin," in that these compounds, apparently without exception, possess the property of yielding phlobaphenes. In respect of this latter group, it is to be noted in connection with the qualitative tests above enumerated that the formation of phlobaphene and of precipitates with bromine water and with formaldehyde sufficiently indicate the presence of this variety of tannin, because these compounds may not all react with pine wood and hydrochloric acid, or diazobenzene chloride, or give protocatechuic acid as one of their decompo-ition products.

There appears to be ample evidence also of the existence of special varieties of glucoside belonging to this third class, distinguished by their extremely hygroscopic nature and the fact that they are insoluble or nearly so in acetic ether. They give, however, the well-marked reactions of the phlobatannins. None of these compounds has yet been obtained in a pure condition, but

when they are digested with boiling dilute mineral acids a sugar and phlobaphene appear to be mainly produced.

Methods of isolation.—All the well-known tannins are dissolved by hot water, and yield precipitates with lead acetate solution, and thus by decomposing the well-washed lead precipitate from a plant infusion in the moist condition with sulphuretted hydrogen a crude solution of the tannin is obtained. This can be concentrated *in vacuo* over caustic potash or sulphuric acid. In the place of lead acetate, stannous chloride was employed by Proust in 1798 (Ann. Chim. Phys., 25, 225), who is credited with being the first to prepare tannic acid in a nearly pure condition. As, however, the tannin usually exists in the plant side by side with yellow colouring matter, either in the free state or as glucoside, and other secondary substances soluble in water, a fractional precipitation with lead acetate is preferably adopted, in which case the middle portion usually yields the purest tannin (Grabowski, Sitz. Ber., 1867, 55, ii., 567; Trimble, "The Tannins," 1892, i., 85). A preliminary treatment with lead acetate in the presence of a little acetic acid is serviceable in some cases for the precipitation of coloured impurities. Probably the solvent most extensively employed since 1880 in the investigation of tannins has been ethyl acetate, in which case it has been usual to agitate a solution of the substance or extract of the plant with this solvent. A preliminary addition of salt or sodium sulphate to the liquid is beneficial.

Certain tannin glucosides, owing to their sparing solubility in ethyl acetate, cannot be satisfactorily isolated in this manner, and the method is not applicable to the case of mineral salts of the tannin, in which the preliminary production and subsequent decomposition of the lead salt is to be recommended. Numerous methods have been adopted for the purification of the tannin thus prepared, and are given under the head of the special substance with which they have been employed.

In many cases it has been found preferable to extract the tannin matter with an organic solvent rather than with water. This is, as a rule, to be advised, as the crude substance is thus more readily isolated in a concentrated form. Indeed, one of the oldest methods of separating tannins from other substances is that of Pelouze (Ann. Chim. Phys., 1834, 55, 337), who exhausted powdered gall-nuts with commercial ether. Various mixtures of alcohol, ether, and water have been recommended, and also dilute alcohol in the case of gall-nuts for preparing gallotannic acid, although these methods must not be considered of special advantage for the isolation of

tannins as a whole. Probably the most efficient solvent for general purposes of investigation is acetone which was employed by Trimble for the percolation of numerous tannin matters ("The Tannins").

I. Depside Group.

Tannin, Tannic acid, Gallotannin, Gallotannic acid is found to the largest extent in galls which arise from the puncture of insects of the genus *Cynips* on the leaves and buds of various species of oak, more especially the *Quercus lusitanica* (Lam.), and on a species of sumach, *Rhus semilata* (Murr.). Aleppo galls, derived from the young shoot of the oak and which are the best variety of oak gall on the market, contain 50—60 per cent. of gallotannic acid, whereas Chinese galls from sumach yield as much as 70 per cent. In smaller amount it occurs also in numerous plants, and is probably the main tannin of various sumachs, of valonia, divi-divi, and algarobilla.

The methods employed for the isolation of gallotannic acid from galls are more or less modifications of that of Pelouze, which consists in extracting finely powdered galls with commercial ether. The extract separates into two layers, the upper consisting of an ethereal solution of gallic acid, wax, and resinous substances, whereas the lower represents a concentrated solution of gallotannic acid which, on evaporation, remains as a porous mass. In place of the ether a mixture of 75 per cent. commercial ether and 25 per cent. alcohol can be employed. The method of Leconnet (Annalen, 1836, 18, 179) consists in stirring powdered galls into ether until a thin cream results, pressing the mixture and repeating the operation until tannin is no longer removed. According to Domine (J. Pharm. Chim., 1844, [3], 5, 231), it is advantageous to allow the powdered galls before extraction to remain for some time in a moist atmosphere, and Pelouze's process with this modification was adopted by the British and United States pharmacopœias.

For the manufacture on the large scale, Chinese or Japanese galls are preferably employed owing to their richness in tannin. The finely powdered material is stirred with sufficient water at 50—60° to form a concentrated aqueous extract, and after filtration the clear liquid is agitated with one-fourth of its volume of ether until an emulsion results. After standing for several days, the upper ethereal liquid which has separated is removed, and the lower layer, which contains all the tannin matter, is run into a still and the ether which is present recovered. After cooling the syrupy liquid is

spread out on sheets of tin, and heated by means of a steam coil, when the gallotannic rapidly puffs up and dries.

Thus prepared the commercial tannin contains some quantity of gallic acid, plant wax, glucose and other impurities; to remove these the material may be washed with ether, or the aqueous solution shaken with ether, or the aqueous liquid fractionally precipitated with common salt, the precipitate dissolved in ethyl acetate, and the tannin recovered by evaporation under reduced pressure. Trimble ("The Tannins," 85) treats a 5 per cent. solution of the tannin with 10 per cent. lead acetate, drop by drop, until the precipitate, at first yellow coloured, ceases to be granular and is colourless. This is collected, the filtrate agitated two or three times with ethyl acetate and the extract evaporated. The colourless product, which still contains gallic acid, is redissolved in water, and the solution, after agitation with ether, evaporated under reduced pressure. Finally, the residue dissolved in ether by the aid of a little water is again brought rapidly to dryness under reduced pressure, and thus obtained is colourless and gives no reactions for gallic acid or glucose. With the object of preparing a homogeneous product, Walden (Ber., 1898, 30, 3154) has employed dialysis, and also the precipitation of a solution of the purest commercial tannin in ethyl acetate with benzene. Rosenheim and Schidrowitz (Chem. Soc. Trans., 1898, 73, 882) point out the extreme difficulty of removing the last traces of gallic acid from the tannin and employ a mixture of ether and acetone for this purpose. Paniker and Stiasny (Chem. Soc. Trans., 1911, 99, 1821) state, however, that the process of Rosenheim and Schidrowitz only partially removes gallic acid. The method suggested by Perkin, which consists in neutralising a solution of the tannin with sodium bicarbonate, extracting the mixture with ethyl acetate, and subsequently precipitating the substance from the extract with benzene, gives a product free from even traces of gallic acid (see also Iljin, Ber., 1909, 42, 1731). Fischer and Freudenberg (Ber., 1912, 45, 919) find the addition of dilute sodium hydroxide to the tannin solution until faintly alkaline before extraction with ethyl acetate is similarly beneficial.

Gallotannic acid as found in commerce consists of an amorphous powder possessing a faint yellow colour, although when exhaustively purified it is colourless. It is readily soluble in water and alcohol, more sparingly in ethyl acetate, insoluble in pure ether, chloroform, or benzene. With solutions of ferric salts, gallotannic acid gives a bluish-black coloration or precipitate, according to the concentration, whereas ferrous salts give with strong solutions only a white precipitate

which gradually turns blue in the air. Many metallic salts give precipitates with the tannin, those of lead and tin being colourless, whereas the copper and silver compounds possess a brown tint. Cold alkaline solutions absorb oxygen from the air and darken in colour with production of the so-called *metagallic acid.* When boiled hydrolysis occurs, gallic acid being formed. Gallotannic acid precipitates most alkaloids and gives precipitates with albumen and gelatin, the latter, according to Trunkel (Zeitsch. Biochem., 1910, 26, 458), in quantitative amount.

Analyses of gallotannin by Berzelius, Pelouze, Mulder, Bijlert, Strecker, Gautier, Trimble, Dekker, and Walden have been in fairly close agreement, varying from about C = 51·5 to C = 52·3; H = 3·7 to H = 4·1 per cent. Iljin (Ber., 1909, 42, 1735) has suggested higher numbers (C = 54·13; H = 3·22), the correctness of which he has again emphasised (J. pr. Chem., 1910, [ii.], 82, 422; *cf.* Nierenstein, *ibid.*, 1909, 42, 3552). Mulder (J. pr. Chem., 1849, 48, 90) was the first to assign to gallotannin the formula $C_{14}H_{10}O_9$, and this was subsequently adopted by Schiff (Ber., 4, 231), and until recently generally accepted as correct. Very numerous salts of gallotannic acid have been described which are in fair agreement with this view, of which *ammonium tannate,* $NH_4C_{14}H_9O_9$, *potassium tannate,* $KC_{14}H_9O_9$, *sodium tannate,* $NaC_{14}H_9O_9$, and *barium tannate,* $Ba(C_{14}H_9O_9)_2$ (Buchner, Annalen, 53, 361) may be given as examples. For a complete list reference should be made to Beilstein (1896, ii., 1926).

Gallotannic acid isolated from plants is said to contain free glucose which is difficult to eliminate. Strecker (Annalen, 90, 340) indicated the possible existence of a glucoside of the formula $C_{27}H_{22}O_{17}$, although Schiff (*ibid.*, 170), while agreeing that unaltered tannin is probably a glucoside of digallic acid, preferred the formula

$$C_{34}H_{28}O_{22}(= C_6H_{12}O_6 + 2C_{14}H_{10}O_9 - 2H_2O)$$

This corresponds to a yield of 23 per cent. of glucose; whereas in natural tannin about 22 per cent. is said to have been detected.

When gallotannic acid is heated at from 160—215°, water, carbon dioxide, and *pyrogallol* are evolved, and a dark coloured non-volatile substance known as metagallic acid is produced. According to Trimble (*loc. cit.*) the best yields of pyrogallol are obtained by raising the temperature slowly to 215° and then keeping it between 190—210° for half an hour. Digested with boiling dilute mineral acids, gallic acid is produced, and Wetherill, who employed for this purpose 50 grams of tannic acid and 500 c.c. of sulphuric acid (1 vol. acid + 4 of water), obtained a yield of 87·4 per cent. of gallic acid. Knop

(Annalen, 170, 44) states he obtained 95 per cent., and Stenhouse the theoretical amount, whereas Trimble (*loc. cit.*) considers that when pure gallotannic acid is heated with a 2 per cent. solution of absolute hydrochloric acid, gallic acid only is produced. This reaction was formerly assumed to be expressed by the following equation :—

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$$

Boiling alkaline solutions also produce gallic acid, but hot aqueous ammonia yields *ammonium gallate* and *gallamide* as follows :—

$$C_{14}H_{10}O_9 + 2NH_3 = C_7H_5O_5NH_4 + C_7H_5O_4NH_2$$

According to Voswinkel (D.R.P., 1905), on adding formaldehyde to an aqueous solution of tannin and carbamide in molecular proportion, a precipitate of *methylene tannin carbamide* is formed—

$$C_{14}H_{10}O_9 + CO(NH_2)_2 + H.CHO = C_{14}H_9O_9.CH_2.NH.CO.NH_2 + H_2O$$

It is a yellow powder decomposing about 220° and is insoluble in organic solvents with the exception of alcohol.

By heating barium gallate with silver nitrate, Löwe (J. pr. Chem., 1867, 102, 111) obtained a substance resembling gallotannic acid, and the same compound, together with ellagic acid, was also produced by the action of arsenic acid on gallic acid. Schiff (Ber., 1871, 4, 231) found that when gallic acid was heated with phosphorus oxychloride at 100°, and subsequently at 120°, digallic acid was produced and this had the same percentage composition, and properties as natural gallotannin. The reaction (Annalen, 1873, 170, 56) most probably occurred as follows :—

$$2C_7H_5O_4(OH) + POCl_3 = 2HCl + \begin{matrix} C_7H_5O_4—O \\ \diagdown \\ \diagup \\ C_7H_5O_4—O \end{matrix}\!\!>POCl$$

$$C_{14}H_{10}O_{10}.POCl + 4C_7H_6O_5 = 3C_{14}H_{10}O_9 + H_3PO_4 + HCl$$

and there was indeed evidence of the intermediate formation of a phosphorus compound. Further, it was noticed that pure tannin gives some ellagic acid when heated with phosphorus oxychloride at 130—140°. Schiff (Ber., 1871, 4, 967) also corroborated Löwe's statement that digallic acid is produced from gallic acid by means of arsenic acid. The reaction could be expressed thus :—

$$C_7H_5O_4(OH) + H_3AsO_4 = C_7H_5O_4.O.AsO_2 + 2H_2O$$

$$\begin{matrix} C_7H_5O_4 \\ \diagdown \\ \diagup \\ AsO_2— \end{matrix}\!\!>O + C_7H_5O_4(OH) + H_2O = \begin{matrix} C_7H_5O_4 \\ \diagdown \\ \diagup \\ C_7H_5O_4 \end{matrix}\!\!>O + H_3AsO_4$$

The following constitution was first assigned by Schiff to his digallic acid :—

$$COOH(OH)_2C_6H_2 . O . C_6H_2(OH)_2COOH,$$

and indeed by means of acetic anhydride only a tetra-acetyl compound was apparently produced. Later (*loc. cit.*, 1873) a study of acetyltannin which was obtained as warty nodules, melting-point 137°—Trimble ("The Tannins," i., 87) gives melting-point 139°; Nierenstein (Collegium, 1905, 23), 129—131°; Dekker (Ber., 1906, 39, 2497), 129°; and Nierenstein (*ibid.*, 1907, 40, 917), 146° (*cf.* Böttinger, *ibid.*, 1884, 17, 1478)—indicated that this possessed the formula $C_{14}H_5O_9Ac_5$, and the constitution given below was therefore adopted—

$$COOH(OH)_2 . C_6H_2 . O . CO . C_6H_2(OH)_3$$

A penta-acetyl derivative was also given by digallic acid prepared both by the phosphorus oxychloride and arsenic methods (Ber., 1873, 68, 72), and there appeared at the time to be no doubt that this artificial product was identical with the natural tannin. Phosphorus pentachloride and phosphorus trichloride again produced digallic acid from gallic acid. According to Geschwender (Inaugural Diss. Munich, 1906), penta-acetyldigallic acid can be obtained in a crystalline condition from dilute alcohol.

By heating protocatechuic acid with arsenic acid, Schiff (Ber., 1882, 15, 2589) obtained his *diprotocatechuic acid* in the form of a hygroscopic glassy mass. This possessed the characteristics of a tannin, and with boiling dilute mineral acids was converted into protocatechuic acid.

Dipyrogallol carboxylic acid from pyrogallol carboxylic acid and *phloroglucinol tannic acid* from phloroglucinol carboxylic acid were also prepared (Annalen, 295, 40).

Freda (Ber., 11, 2033; 12, 1576), however, did not obtain digallic acid by the interaction of gallic and arsenic acids, but only an arsenic compound, which on treatment with sulphuretted hydrogen gave gallic acid.

Biginelli (Gazzetta, 1909, 39, ii., 68) obtained from arsenic acid and gallic acid *arsenic gallic acid*, $AsO(OH)_2O . C_6H_2(OH)_2COOH$, *arsenic digallic acid*, $(OH)AsO[O . C_6H_2(OH)_2COOH]_2$, and *dihexahydroxybenzophenone arsenic acid*,

$$(OH)AsO[O . C_6H_2(OH)_2 . CO . C_6H_2(OH)_3]_2$$

The second of these compounds, Biginelli suggests, forms one of the constituents of Schiff's artificial tannin.

Similar compounds are produced by the action of phosphoryl chloride or antimonic acid on gallic acid (Biginelli, *ibid.*, 283) to which the following formulæ have been assigned:—

$$PO(O.C_6H_2(OH)_2COOH)_3,\ SbO(OH)_2O.C_6H_2(OH)_2COOH,$$
and $$(OH)SbO(O.C_6H_2(OH)_2COOH)_2$$

All these substances react as tannins, and it seems possible that Schiff's digallic acid preparations are in reality similarly constituted. On the other hand, Walden (Ber., 1898, 81, 3168) prepared Schiff's digallic acid by the arsenic acid method, and although he noted the difficulty of completely removing arsenic, this appeared to be absent from the purified compound (*cf.* also Nierenstein, Chemie der Gerbstoffe, Stuttgardt, 1910, 44).

By heating gallotannin with benzoyl chloride, Böttinger (Ber., 1889, 22, 2707) prepared a *benzoyltannin* in the form of a sandy light yellow coloured powder. Sisley (*loc. cit.*) and Dekker (*loc. cit.*) describe similar products. Vournasos ("Le tannin de la noix de galle," 27), on the other hand, describes *pentabenzoylgallotannin* as a well-defined crystalline compound.

By heating a mixture of ethyl gallate and pyruvic acid with sulphuric acid, Böttinger (Ber., 1884, 17, 1476) prepared a substance $C_{14}H_{10}O_9$, $2H_2O$, which he at first regarded as digallic acid. It consisted of a very hygroscopic mass which had the properties of a tannin, gave a penta-acetyl compound, and with lead acetate solution yielded a dull yellow precipitate. As, however, by digestion with boiling dilute hydrochloric acid no gallic acid was produced, it could only be an isomeride of natural gallotannin.

According to Hunt (Chem. News, 52, 49), a substance which behaves in many respects like tannin can be prepared by the interaction of monobromoprotocatechuic acid and potassium gallate—

$$C_6H_2(OH)_3COOK + C_6H_2Br(OH)_2COOH = C_6H_2(OH)_3CO.O.C_6H_2(OH)_2COOH + KBr,$$

but Schiff (Gazzetta, 1897, 21, i., 90) was unable to synthesise tannin by this method.

Herzig and Tscherne (Ber., 1905, 38, 989) obtained *methyltannin* by the action of diazomethane on gallotannin suspended in ether, and describe it as a colourless amorphous powder, melting-point 124—126°. It had the composition

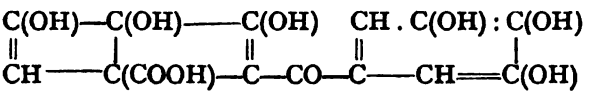
$$C_{24}H_8O_7(OCH_3)_8 \text{ or } C_{24}H_{10}O_7(OCH_3)_8$$

is dextro-rotatory and when hydrolysed gives a mixture of *trimethylgallic acid* and 3 : 4-*dimethylgallic acid*. The percentage of methoxyl

found, however, approximates to that required for a pentamethylgallotannin (Herzig, *ibid.*, 1908, 41, 83). Later, Herzig and Renner (Monatsh., 1909, 30, 543) consider that their methyltannin may possibly be a mixture of substances which have approximately the same composition, and indeed contain pentamethoxy derivatives of the tannin constituents described by Nierenstein (see below). Rosenheim (Chem. Soc. Proc., 1905, 21, 157), by means of methyl sulphate, obtained a compound having the composition of a tannin pentamethyl ether.

Whereas, for a considerable time, Schiff's formula was generally recognised as the best-known expression for the constitution of gallotannin, it had been pointed out by Scheibler in 1866 (Zeitsch. Zuckerind., 16, 33), by van Teigheim in 1867 (Ann. Sci. Nat., [v.], 8, 210) and by Gunther in 1872 (Ber. pharm. Ges., 5, 172) that natural gallotannin was optically active.

Owing no doubt to the idea that unless carefully purified, gallotannin obstinately retains traces of sugar, this fact did not attract special attention until Schiff (Gazzetta, 1895, 25, ii., 437) noted that the pure substance possesses a dextro-rotation ($[\alpha]_D$ = + 14° to + 67°). In order to provide for the assymmetric carbon atom, a modification of his earlier formula was accordingly necessary, and he now suggested that gallotannin should be represented as a ketonic compound of the following constitution :—



On the other hand, by the action of phenylhydrazine under varied conditions, no hydrazone could be prepared from gallotannin.

According to Walden (Ber., 1897, 30, 3151), who examined the purest samples of commercial tannin available, these products, as already indicated by Schiff, vary considerably in optical activity, having $[\alpha]_D$ from + 15° to + 67°, and are evidently mixtures.

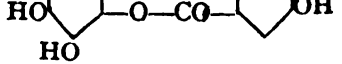
Whereas Paterno (Zeitsch. physikal. Chem., 1899, 4, 458) found the molecular weight of tannin in water to be 2643—3700, and that of Schiff's digallic acid 660, Sabanéeff (J. Russ. Phys. Chem. Soc., 1890, 22, 104) showed that in acetic acid gallotannin gave the figure 1322. Kratff, again (Ber., 1899, 32, 1613), found for gallotannin in water 1587—1626.

Walden (Ber., 1899, 31, 3167), on the other hand, showed that the molecular weight indicated by Schiff's digallic acid in boiling acetone is about 316, whilst samples of Merck's and Schuchardt's

tannin in the same solvent respectively gave figures of 753—763 and 1350—1360. Moreover, the affinity coefficient of Schiff's digallic acid is K = 0·0012, whereas that of tannin, which varies greatly with the concentration, is from K = 0·0001 to K = 0·00006. Spectrometric examination of solutions of gallotannin and digallic acid showed also that their absorption powers for all regions of the spectrum are entirely different, and from these facts there could be no doubt that gallotannin and Schiff's digallic acid are distinct compounds. Moreover, it was not possible to regard digallic acid as the inactive modification of gallotannin. Rosenheim and Schidrowitz (Chem. Soc. Trans., 1898, 73, 878), who examined samples of commercially "pure" gallotannins, again pointed out the wide limits through which the rotation of these varied, the minimum being $[\alpha]_D$ + 11° and the maximum + 74·2°. The important point was also indicated that these commercial products could be separated into fractions the rotatory powers of which varied from $[\alpha]_D$ ± 0° to $[\alpha]_D$ + 75·2°, and it was further concluded that in each of the original samples a homogeneous gallotannin exists, possessing an optical activity of about $[\alpha]_D$ + 75°. As a confirmation of this point it was noted that the quinine salts and penta-acetyl compounds prepared from gallotannins of $[\alpha]_D$ + 11° up to $[\alpha]_D$ + 75° were identical in rotatory power *inter se* with those prepared from the purified gallotannin (*cf.* also Iljin, Ber., 1914, 47, 985).

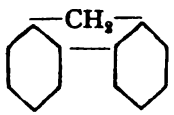
According to Nierenstein (Ber., 1905, 38, 3641) when gallotannin is distilled with zinc-dust, diphenylmethane is produced, a result which is in harmony with Schiff's formula for digallic acid, in that it has been previously found that ellagic acid (1) and diphenylmethylolid (2) (Graebe, *ibid.*, 1903, 36, 212) by a similar method give fluorene (3) (*cf.* also Perkin and Nierenstein, Chem. Soc. Trans., 1905, 87, 1412):—

(1)

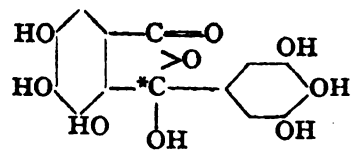


(2)

(3)

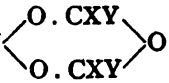


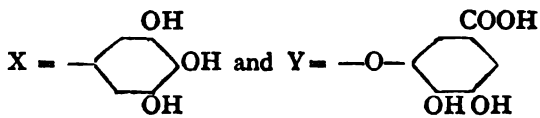
Dekker (Ber., 1906, 39, 2497; *ibid.*, 3784) suggested that gallotannin should be represented as a derivative of phthalic anhydride—



and it was considered that this formula is in harmony with the optical activity, almost complete hydrolysis to gallic acid and the formation of diphenylmethane. According to numerous workers, however, gallotannin gives only a penta-acetyl derivative, whereas such a constitution indicates seven hydroxyl groups, and though Dekker describes a hexa-acetyl tannin $[\alpha]_D$ + 64·4° the existence of this is doubtful.

Later, however, Dekker (De Looistoffen, 1908, ii., 30, 1908) was unable to confirm the production of diphenylmethane from tannin as observed by Nierenstein (*loc. cit.*), and obtained only diphenyl. Nierenstein (Chemie der Gerbstoffe, 1910, 47), however, maintains the correctness of his former work.

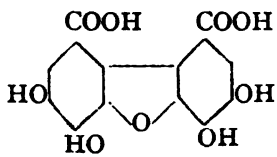
Lloyd (Chem. News, 1908, 97, 133) concludes that gallotannin contains three digallic groups united to each other to form a six-membered ring of the type  in which



Nierenstein (Ber., 1907, 40, 916) separates acetylgallotannin, which, on analysis, behaves as a penta-acetyl compound, into two amorphous components, (*a*) melting-point 203—206°, present in small quantity, and (*b*) the main product, melting-point 166°. The former when hydrolysed gives gallic acid, and on oxidation by means of potassium persulphate and acetic acid, ellagic acid. By means of zinc-dust the penta-acetyl tannin, melting-point 203° (Ber., 1908, 41, 77), may be reduced to the acetyl derivative, melting-point 166°. Again, the compound, melting-point 166°, which is termed *acetyl-leucotannin*, is not a fully acetylated compound, but on further treatment gives hexa-acetyl-leucotannin, melting-point 159°. Thus gallotannin is considered to be a mixture of digallic acid and leucotannin, $C_6H_2(OH)_3.CH(OH).O.C_6H_2(OH)_2COOH$, the latter being evidently the main component of the mixture.

Penta-acetyl-leucotannin (Ber., 1909, 42, 1122) is hydrolysed by boiling dilute sulphuric acid with formation of *gallic aldehyde* and *gallic acid* as its formula suggests, and when oxidised with persulphate and sulphuric acid in boiling acetic acid gives, in addition to ellagic acid, a red amorphous product, *purpuro-tannin* (C = 69·14, H = 2·84), which on distillation with zinc-dust yields naphthalene.

In a later paper (Nierenstein, Annalen, 1912, 386, 318) the formula $C_{14}H_8O_9$ (C = 52·5; H = 2·5) is assigned to this compound, and the *quinoline* salt, $C_{14}H_8O_9 . 2C_9H_7N$, *tetra-acetyl* compound, melting-point 324—327°, *tetrabenzoyl* compound, melting-point 279—281°, and *tetramethylether*, melting-point 242—244°, are described. By distillation with zinc-dust it gives *diphenylene* and not naphthalene, as was at first considered to be the case. With piperidine at 180° it gives 1 : 2 : 7 : 8 *tetrahydroxydiphenylene oxide*, $C_{12}H_8O_5$, melting-point 334—338°, with hydriodic acid and phosphorus *diphenylene oxide*, and from these results appears to possess the following constitution :—

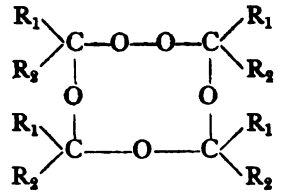


Iljin, on the other hand, who studied the action of zinc-dust on a boiling 10 per cent. aqueous solution of tannin for 15 to 20 hours, obtained an amorphous substance which has $[\alpha]_D^{18·4}$ + 24·1° in 95 per cent. alcohol, gives coloured precipitates with metallic salts, and gallic acid without gallic aldehyde when heated with 20 per cent. sulphuric acid in a current of hydrogen (J. pr. Chem., 1909, [ii.], 5, 80, 332).

According also to Herzig and Renner (Monatsh., 1909, 30, 543), tannin methyl ether (*loc. cit.*) is practically unaffected by boiling with acetic acid, zinc, sodium acetate, and acetic anhydride, no leuco compound being thus produced.

Iljin (J. Russ. Phys. Chem. Soc., 1908, 39, 470; Chemie der Gerbstoffe, 1910, 49) obtained two phenylhydrazine derivatives, $C_{74}H_{58}N_6O_{30}$ and $C_{98}H_{82}N_{14}O_{26}$, from gallotannin. He suggests for gallotannin the formula $C_{56}H_{40}O_{33}$, and proposes the following constitution, in which

R_1 = —CO . $C_6H_2(OH)_3$ and R_2 = —$C_6H_2(OH)_3$:—

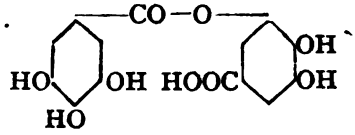


E. Fischer (Ber., 1908, 41, 2875), by coupling tricarbomethoxygallyl chloride with dicarbomethoxygallic acid, obtained a product which, on hydrolysis, gave a substance, melting-point 275—280°, crystallising in prisms or needles. This was considered to be possibly a mixture of digallic acid with gallic acid, but was subsequently shown (1911, see below) to be a slightly impure *digallic acid*,

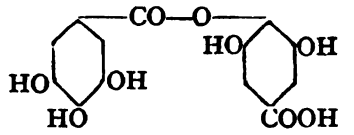
$$(OH)_3C_6H_2 . CO . O . C_6H_2(OH)_2COOH$$

According to Nierenstein (Ber., 1910, 43, 628), by converting gallotannin into the carboethoxy derivative, hydrolysing this with pyridine and repeating the operation three or four times, there is obtained a digallic acid, $C_{14}H_{10}O_9$, $2H_2O$, crystallising in small needles from alcohol and water (1 : 3) which sinters at 214° and melts at 268—270°. It (1) is optically inactive, when hydrolysed gives gallic acid, and on oxidation with hydrogen peroxide ellagic acid, but is not identical with Fischer's digallic acid (2) which does not yield ellagic acid. Nierenstein formulates these compounds as follows :—

(1)



(2)



Penta-acetyldigallic acid, needles, melting-point 211—214°, *penta-benzoyldigallic acid*, needles, melting-point 187—189°, *pentacarbethoxydigallic acid*, small cubes, melting-point 194—195°, and *sodium digallate* are described.

By digestion with boiling acetic anhydride and zinc-dust, penta-acetyldigallic acid gives dl-*hexa-acetyl-leucotannin*, melting-point

154—155°, cubes, and may be separated by means of the strychnine salt into l-*hexa-acetyl-leucotannin*, having melting-point 151° and $[\alpha]_D^{25}$ – 4·6, and d-*hexa-acetyl-leucotannin*, having melting-point 153—154° and $[\alpha]_D^{20}$ + 121·5°.

Iljin (J. pr. Chem., 1910, [ii.], 82, 422) redetermined the molecular weight of specially purified gallotannin in acetone, and found values of 1247—1637, confirming the results of Sabanéeff and of Walden (*loc. cit.*). Accordingly he considers that gallotannin must consist largely of a complex derivative of gallic acid, distinct from the digallic acid and leucotannin of Nierenstein.

When gallotannin is boiled for four hours with zinc oxide the filtrate does not react with ferric chloride. The residue decomposed with sulphuric acid gives gallic acid and the compound previously obtained by the action of zinc-dust on tannin (*loc. cit.*) in approximately equal amount (Iljin, *ibid.*, 1910, [ii.], 81, 327). Manning (J. Amer. Chem. Soc., 1910, 32, 1312) prepares *ethyl gallotannate*, $C_{51}H_{52}O_{26}$, $5H_2O$, yellow crystals, melting-point 157°, by passing dry hydrogen chloride into an alcoholic solution of gallotannin; this on hydrolysis gives ethyl alcohol, dextrose, and gallic acid. This compound may be synthesised by treating a mixture of ethyl gallate and dextrose with phosphoryl chloride.

Fischer and Freudenberg (Annalen, 1911, 384, 225) coupled dicarbomethoxygallic acid and tricarbomethoxygallyl chloride in alkaline solution, and by hydrolysis of the resulting product obtained a pure *digallic acid*. It crystallises in needles, is much less sparingly soluble in water than gallic acid (approximately twelve times), and melts at 275° (corr. 282°) with decomposition. With ferric chloride it gives a blue-black coloration and possesses the properties of a tannin. For a description of the diprotocatechuic acid, digentisic acid, and di-β-resorcylic acid of these authors, see below.

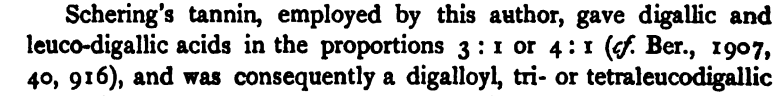
Paniker and Stiasny (Chem. Soc. Trans., 1911, 99, 1819) investigated the acid character of this substance by the diazo-acetic ester method of Fraenkel (Zeitsch. physikal. Chem., 1907, 60, 202), because, according to the previously expressed view of Böttinger (Ber., 1884, 17, 1503), Dekker (*ibid.*, 1906, 39, 2497), and Walden (*ibid.*, 1898, 31, 3170), no free carboxyl group is present in this compound. It is shown that gallotannin is to be regarded as an acid, the affinity constant being of a distinctly higher order than that shown by phenols.

Gallotannin can be divided into two parts by saturating its solution with sodium bicarbonate, one part being soluble in ethyl acetate,

whilst the other forms a sodium salt and is insoluble. Thus the former product is shown to be only half as acid as that which is set free on acidifying the sodium salt in solution. The experiments favoured the view of Kunz-Krause (Schweiz. Wochensch. Chem. Pharm., 1898, No. 38), Walden (*loc. cit.*), Aweng (Rev. Int. Falsif., 1898, 11, 29), and Nierenstein (*loc. cit.*), that gallotannin is a mixture of two or more chemical individuals.

With alcoholic potassium acetate, gallotannin gives a precipitate of the potassium salt which appears to have the unimolecular formula $C_{14}H_9O_9K$. This compound is devoid of optical activity.

According to Nierenstein (Annalen, 1912, 388, 223), when an aqueous solution of tannin is reduced with zinc-dust by Iljin's method (*loc. cit.*), dl-*leucodigallic acid*, fine needles, melting-point 278—280°, is produced, and the same compound can also be prepared by the reduction of digallic acid. By means of the carbethoxy derivative, this can be resolved into l-*leucodigallic acid*, melting-point 276—277°, which has $[\alpha]_D^{15}$ − 70·26°, and d-*leucodigallic acid*, melting-point 276—277°, which has $[\alpha]_D^{19}$ + 104·2° in water. As leucodigallic acid does not possess tanning property, it cannot be present in gallotannin, and the author now therefore discards his theory that the latter is composed of a mixture of digallic and leucodigallic acids. Tannins are accordingly now considered to consist of *polydigalloyl-leuco-digallic anhydrides*—



Schering's tannin, employed by this author, gave digallic and leuco-digallic acids in the proportions 3 : 1 or 4 : 1 (*cf.* Ber., 1907, 40, 916), and was consequently a digalloyl, tri- or tetraleucodigallic anhydride. For further details the original paper must be consulted.

E. Fischer and Freudenberg (Ber., 1912, 45, 915) take an entirely different view of the constitution of gallotannin, and announce the important fact, not generally suspected, that this compound contains a *glucose* nucleus. Purified preparations of gallotannin have $[\alpha]_D^{20}$ approximately + 70°, and these samples, when hydrolysed with acid, yield gallic acid and a small amount of dextrose. Gallotannin is most probably a compound of dextrose with five molecules of digallic acid, of the nature of penta-acetyldextrose, and such a con-

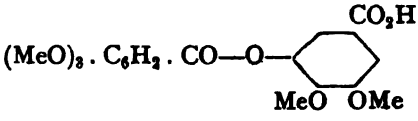
stitution will agree with its high molecular weight, optical activity, faint acidity, and ready solubility in water. Synthetical tannin compounds, derivatives of dextrose, are described, the properties of which favour this suggestion. Tricarbomethoxygalloyl chloride in chloroform solution reacts with dextrose in the presence of quinoline, to form penta-tricarbomethoxygalloyl glucose, from which, by hydrolysis with alkali, *pentagalloyl glucose* is produced. It is a yellow powder of astringent taste, possesses the power of precipitating gelatin solutions, and has $[\alpha]_D$ + 31° to + 35° in water, or + 44·4° in alcohol. Similar compounds of gallic acid with *a*-methylglucoside and glycerol, and of *p*-hydroxybenzoic acid with dextrose are also described.

Manning and Nierenstein (Ber., 1912, 45, 1546) considered that a sugar nucleus is not present in pure gallotannin, and point out that this is not produced when either Schering's tannin or Herzig and Renner's methyl tannin (*loc. cit.*) is hydrolysed with alkali. Again, ethyl gallate is the sole product of the esterification of this tannin.

Herzig (Ber., 1912, 45, 1985) considers that the argument of these authors is no proof of the absence of a sugar nucleus in methyl tannin or tannin itself, whereas Biddle and Kelley (J. Amer. Chem. Soc., 1912, 34, 918) show that the so-called ethyltannate of Manning is in reality ethyl gallate. On the other hand, Feist reiterated the fact (Ber., 1912, 45, 1493) that in 1908 (Chem. Zentr., 1908, ii., 1352) he isolated *glucogallic acid*, a compound of gallic acid and glucose, from Turkish gall-nuts.

Fischer and Freudenberg (Ber., 1912, 45, 2709) further supported their view that gallotannin is a pentadigalloyl glucose, and in continuation of their syntheses of tannin compounds employed pentamethyl-*m*-digalloyl chloride with interesting results. Whereas the digallic acid previously synthesised by these authors is the *p*-compound (Ber., 1910, 43, 628), gallotannin is derived from the *m*-acid, for Herzig has shown that methyl tannin, when hydrolysed, gives gallic acid trimethyl ether and 3 : 4 gallic acid dimethyl ether (*cf.* also Nierenstein).

When the trimethyl ether of galloyl chloride reacts with 3 : 4 gallic acid dimethyl ether, according to the method employed by these authors, *pentamethyl*-m-*digallic acid*—

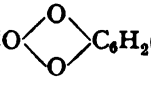


melting-point 192—193°, is produced (*cf.* Mauthner, Ber., 1905, 38, 389; Monatsh., 1909, 30, 543), and from this the chloride, melting-point 109—110°, is readily obtained. In the presence of quinoline, this is condensed with α- and β-glucose respectively, and such a procedure was adopted, because it was found that benzoyl and cinnamyl chlorides, in a similar manner, give with α- and β-glucose stereo-isomeric compounds.

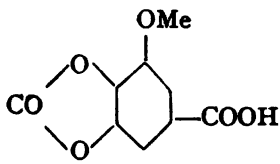
The *m*-digalloyl derivatives thus prepared are amorphous, possess the composition of penta-[pentamethyl-digalloyl]-glucose, but appear in each case to be a mixture of stereo-isomerides. Thus the α-glucose product in acetylene tetrachloride had $[\alpha]_D$ + 28° (approx.), and after repeated solution in hot alcohol $[\alpha]_D$ + 14° (approx.), whereas the β-glucose compound $[\alpha]_D$ + 19·5° behaved similarly.

In case gallotannin is penta-*m*-digalloyl glucose it is evident that this product will represent its methyl ether, and indeed a very close resemblance appears to exist between this substance and the preparation of Herzig. The methyl ether prepared from natural tannin (Herzig, *loc. cit.*) is not a uniform substance, but probably also a mixture of stereo-isomerides, the sample employed having in acetylene tetrachloride $[\alpha]_D^{26}$ + 14°, and after repeated solution in acetone and methyl alcohol $[\alpha]_D^{21}$ + 10·6°. Finally, the criticisms of Manning and Nierenstein (*loc. cit.*) as to the absence of glucose in pure tannin are shown to be valueless. It is likely that the work of Fischer and Freudenberg may soon culminate in the synthesis of penta-*m*-digalloyl glucose itself, in which case it is to be hoped that the mystery which has so long enshrouded the constitution of this important compound will be finally dispersed. On the other hand, the elaborate results of Nierenstein on such a basis are at present difficult to comprehend.

Nierenstein (Ber., 1914, 47, 891) has withdrawn his criticism of Fischer's proposals concerning the structure of tannin, and from the behaviour of tannin with yeast now concludes that glucose is an essential constituent of tannin.

A summary of the position of the chemistry of tannin has been published by Fischer (Ber., 1913, 46, 3253), whilst further steps towards the synthetic production of tannin products have also been taken by him. These include the development of an improved process for the preparation of *m*-digallic acid in quantity (Fischer and Freundenberg, Ber., 1913, 46, 1116). To this end gallic acid was converted into carbonyl-gallic acid,  , by

the action of carbonyl chloride, in the presence of alkali or pyridine, and from this the methyl ether was produced which has the structure—



This product readily condenses with tricarbo-methoxy-galloyl chloride in alkaline solution, and by removal of the carbonic acid residues from the resulting product, a yield of over 50 per cent. of *m*-digallic acid may be obtained.

A number of other synthetic products of this nature have also been described by Fischer (*cf.* Ber., 1914, 47, 2485).

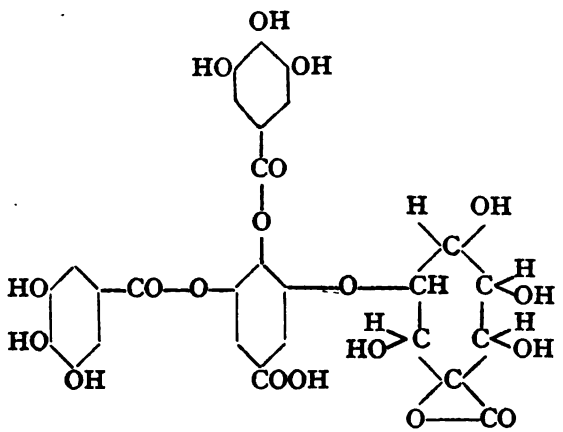
For further references to *gallotannin* see Harnack (Arch. Pharm., 1896, 234, 537), colour reaction; Ljubavin (J. Russ. Phys. Chem. Soc., 1901, 33, 680), tannin and tartar emetic; Thibault (Bull. Soc. Chim., 1903, (iii.), 29, 745), tannin and bismuth; Vigneron (J. Pharm. Chim., 1906, (vi.), 23, 469), iodotannin; Farbewerke vorm. Meister, Lucius, and Brüning (D.R.P. 173729), mixed anhydrides of tannic and cinnamic acids; Biginelli (Gazzetta, 1907, 37, ii., 205; *ibid.*, 1903, 38, i., 559), tannates of quinine; Hildebrandt (D.R.P. 188318), tannin and formaldehyde; Francis and Nierenstein (Collegium, 1911, 335), action of benzoyl chloride and potassium cyanide on benzoyl-hydroxybenzoic acids and on acetylated hydroxybenzoyl-hydroxybenzoic acids; Nierenstein (Die Gerbstoffe).

Chestnut tannin.—Chestnut tannin has been examined by Nass (Inaugural Diss., 1884, Dorpat, Russia) and by Trimble ("The Tannins," ii., 119). According to the latter author it is probably identical with ordinary gallotannin (see Chestnut extract).

Chebulinic acid or Eutannin.—This tannin was isolated by Fridolin from myrobalans, *Terminalia chebula* (Retz.), which also contain an ellagitannin. It crystallises in rhombic prisms, is sparingly soluble in cold water, gives with ferric chloride a blue-black precipitate, and by heating with water is converted into gallic acid and a new tannin.

Thoms (Chem. Zentr., 1906, i., 1829; Apotheker Zeit., 1906, 21, 354) has found that commercial *eutannin* is identical with chebulic acid, $C_{28}H_{22}O_{19}$. It consists of small colourless needles, containing water of crystallisation, reacts acid to litmus paper, decomposes at 234°, and has $[\alpha]_D$ initially + 61·7°, gradually rising to + 66·9°. An

ennea-acetyl and *methyl* derivative are described, the latter giving trimethylgallic acid by the action of sodium hydroxide solution. With water at 100—150° the tannin yields gallic acid and *eutannin hydrate*, $C_{28}H_{24}O_{20}$, a colourless powder decomposing at 200—210°. When eutannin is dissolved in cold sodium hydroxide, the solution acidified with acetic acid, and then treated with lead acetate solution, the resulting precipitate, after decomposition with sulphuretted hydrogen, gives gallic acid, and a tannin $C_{14}H_{16}O_{12}$ or $C_{14}H_{14}O_{11}$, which consists of a yellow powder, having $[\alpha]_D$ + 26° at 15°, and giving a blue coloration with ferric chloride. To chebulinic acid the following constitution is assigned :—



According, however, to Fischer and Freudenberg (Ber., 1912, 45, 915), when hydrolysed chebulinic acid gives also dextrose.

Hamamelitannin.—This compound, one of the few gallotannins as yet isolated in a crystalline condition, occurs in the bark of the *Hamamelis virginiana* (Linn.), a tree, 10 to 12 feet high, common in North America. The bark, previously extracted with light petroleum to remove plant wax, is exhausted with ether-alcohol (5 : 1), the solution evaporated, the residue dissolved in a little alcohol and treated with ether to precipitate certain impurities. Evaporation of the ethereal liquid gives a product, a hot aqueous solution of which, after treatment with alumina and animal charcoal, deposits, on cooling, the substance in the form of small colourless needles. From a dilute aqueous solution, hamamelitannin, $C_{14}H_{14}O_9$, crystallises with $5H_2O$, but deposited from strong solutions the crystals contain $2\frac{1}{2}H_2O$. The air-dried substance melts at 115—117°, although when dried at 100° the melting-point is 203°. Hydrolysed with boiling

dilute sulphuric acid, gallic acid only was produced, and the presence of a sugar could not be detected. Hamamelitannin is dextro-rotatory, $[\alpha]_D = +35{\cdot}43°$. According to Fischer and Freudenberg (Ber., 1912, 46, 2712), however, this tannin probably contains a sugar nucleus.

Benzoylhamamelitannin, $C_{14}H_9O_9(C_7H_5O)_5$, is a yellow powder which melts at about 125—132° (Grüthner, Arch. Pharm., 236, 303).

Oak wood tannin is probably a member of this group, but is described under the heading of *Phlobatannins*.

Sumach tannin (see Sumach).

Diprotocatechuic acid is prepared by coupling monocarbomethoxyprotocatechuic acid with dicarbomethoxyprotocatechuyl chloride in alkaline solution and subsequently hydrolysing the product. It possesses the constitution $(OH)_2C_6H_3 . CO . O . C_6H_3(OH)COOH$, and consists of fine needles which begin to sinter at 230° and melt with decomposition at 237—239°. It is much more sparingly soluble in water than protocatechuic acid, gives with ferric chloride a bluish-green coloration, and possesses tanning properties (Fischer and Freudenberg, Annalen, 1911, 384, 2, 238).

Di-β-resorcylic acid, prepared from β-resorcylic acid by the same general method, $(OH)_2C_6H_3 . CO . O . C_6H_3(OH)COOH$, forms small microscopic needles, melting at 215° (corr.), sparingly soluble in water. It gives with ferric chloride a violet-red coloration and behaves as a tannin.

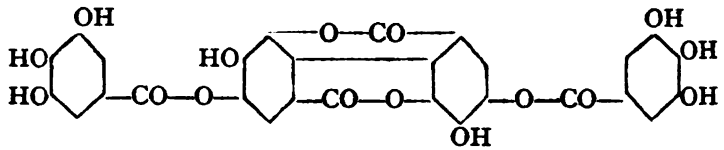
Digentisic acid, $(OH)_2C_6H_3 . CO . O . C_6H_3(OH)COOH$, crystallises in fine needles, melting-point 208—209° (corr.), sparingly soluble in water. The aqueous solution precipitates gelatin and gives a blue coloration with ferric chloride.

Fischer and Hoesch (*loc. cit.*, 224) and Fischer and Lepsius (*loc. cit.*, 224) have prepared numerous other acids of this type, but it is not stated as yet if these are to be regarded as tannins. Lecanoric acid, ramalic acid, evernic acid, and no doubt other lichen acids (*loc. cit.*) which structurally belong to this group may, it is possible, also possess tanning property.

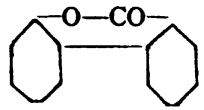
Group II.—Diphenylmethylolid or Ellagitannins.

This tannin group, which has for its mother substance diphenylmethylolid (2), is at present only represented by one well-authenticated member known as ellagitannin, unless indeed pomegranate tannin (see below) is a distinct compound. Whereas Perkin and Nierenstein (Chem. Soc. Trans., 1905, 87, 1428) considered that ellagitannin was probably formed by the condensation of two molecules of digallic acid and possessed the formula (1) or was a glucoside

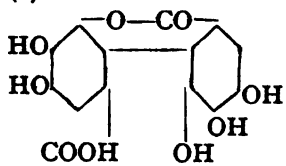
of this substance, according to Nierenstein, ellagitannin (*q.v.*) (*cf.* also Ber., 1912, 45, 365) is a glucoside of luteoic acid (3)—



(1)



(2)



(3)

Numerous natural tannin matters yield ellagic acid, but these have been little investigated, and it is likely that glucosides giving ellagic acid by hydrolysis but differing from ellagitannin itself in the character of their sugar nuclei will be later discovered.

Though various hydroxydiphenylmethylolid compounds have been synthetically prepared, *e.g.* metellagic acid, $C_{15}H_5O_4(OH)$, catellagic acid, $C_{14}H_4O_4(OH)_2$, flavellagic acid, $C_{14}HO_4(OH)_5$, and coeruleoellagic (cyanellagic) acid, $C_{14}O_4(OH)_6$, (*loc. cit.*), ellagic acid is the only member of this group which has been isolated from natural sources.

Pomegranate tannin, $C_{20}H_{16}O_{13}$, is an amorphous greenish-yellow substance contained in the root bark of *Punica granatum* (Linn.). Boiling dilute sulphuric acid hydrolyses it with formation of a sugar and ellagic acid (Rembold, Annalen, 143, 385).

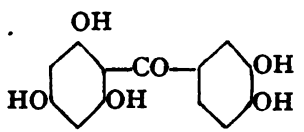
Group III.—Catechol or Phlobatannins.

The catechol tannins are characterised among other distinctive features by the important fact that when digested with boiling dilute mineral acids a red precipitate, known as "anhydride" or "phlobaphene," is produced. The designation "catechol" arises from the fact that the majority of these substances give a green coloration with ferric chloride, and protocatechuic acid or catechol as one of their decomposition products. Such a classification is, however, misleading, in that by comparison with gallotannin, one is led to infer that these substances are similarly constituted and derived from diprotocatechuic acid only—

$$(OH)_2C_6H_3 . CO . O . C_6H_3(OH)COOH$$

When hydrolysed, however, diprotocatechuic acid gives two molecules of protocatechuic acid without production of phlobaphene (Emil Fischer, private communication). Moreover, certain phlobaphene-yielding compounds are now known to exist in which a catechol nucleus is absent. Thus the cyanomaclurin of Jakwood (*q.v.*) is an instance in point, for although it contains only phloroglucinol and resorcinol nuclei, it readily yields a red anhydride of this character (*cf.* also Mimosa tannin, Pistachia tannin, and Maletto tannin). Evidently therefore the phlobaphene reaction is either due to the special structure of the tannin itself, or to the presence of a second phenolic grouping other than catechol in the molecule. This structure may perhaps vary in certain cases, but until this is clear it appears to be preferable to include all phlobatannins under one group rather than to complicate the subject by the introduction of subdivisions.

Böttinger and Etti (*loc. cit.*) have suggested a benzophenone structure for certain tannins, and this applied to the phlobatannins has, at first sight, the merit that *maclurin* (see Old Fustic)—



with dilute hydrochloric acid gives rufimoric acid (Wagner, Jahres., 1851, 420), a red amorphous phlobaphene-like mass. *Kinoin* (see Kino), usually regarded as the methyl ether of a pentahydroxybenzophenone, is readily transformed into kino-red, whereas *aromadendrin* (see Kino), apparently also a benzophenone derivative, resembles, according to Maiden and Smith, *catechin* in many of its properties. It has not yet been ascertained if the carboxylic acids of certain hydroxybenzophenones are tannins, but on the other hand it is to be remembered that compounds possessing such a structure will be strong mordant dye-stuffs, a property which is generally absent from tannins of the so-called catechol type. As already indicated, many phlobatannins are known which contain two distinct nuclei, more frequently phloroglucinol in addition to catechol, a fact which in these cases accounts for their reactivity with diazobenzene. More difficult to understand, however, is the precipitation of all phlobatannins in aqueous solution with bromine; this could be accounted for in those instances in which phloroglucinol or resorcinol nuclei are present in the compound, but curiously enough no difference in this respect appears to have been observed in cases where evidence as to the existence of these latter

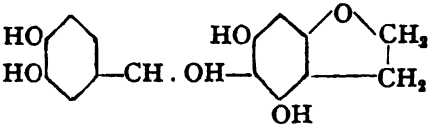
groupings has been of a negative character. Though by incautious alkali fusion, the existing phloroglucinol nucleus may escape detection and probably in many instances has done so, this evidence is such that it is hard to presume that in all cases bromine precipitation arises from the presence in these compounds of a specific phenolic grouping.

It is most probable that the phlobaphene reaction is, in many cases, to be assigned to the well-known reactivity of the phloroglucinol group present in these substances, and this has also been suggested by Emil Fischer. Thus coloured compounds can be obtained by the interaction of phloroglucinol with many aldehydes, of which the red phloroglucinol vanillein is an example, and moreover the phloroglucides of Counder (Ber., 1895, 28, 26), prepared by passing hydrogen chloride into mixtures of phloroglucinol and various sugars in aqueous solution, are coloured, the *d*-galactose phloroglucide possessing a red tint. Again, by boiling dextrose and phloroglucinol with dilute hydrochloric acid, a brownish-red precipitate of a phlobaphene-like character can be easily produced (private communication). Interesting in this respect also is the "phlorotannin red" of Schiff (Annalen, 245, 40), which he obtained by heating his so-called diphloroglucinol carboxylic acid to 160—175°.

That phlobatannins like gallotannin owe their tanning property, as a rule, to the depside grouping appears likely, and it has indeed been observed by Trimble ("The Tannins," ii., 91) that tannins from various species of oak, on long digestion with boiling 2 per cent. hydrochloric acid, give not only phlobaphene but some quantity of protocatechuic acid.

In the light of the researches of E. Fischer and Freudenberg (*loc. cit.*), it is also to be anticipated that many of these compounds will be eventually found to possess a sugar nucleus.

Closely connected with the phlobatannin group are the well-defined crystalline substances catechin, aca-catechin and cyanomaclurin, to the first of which the constitution—



has been assigned by v. Kostanecki and Lampe.

Catechin, although not a tannin, reacts with pine wood and hydrochloric acid, gives with bromine water the insoluble bromcatechuretin and readily yields substances of a phlobaphene character.

Though the evidence is not precise it is stated by Loewe and also by Etti that catechin can be readily transformed into catechutannic acid, a substance existing side by side with it in the plant and possessing properties typical of the phlobatannin group. It has indeed been surmised that the catechol tannins of certain plants may owe their origin to the prior existence of substances of the catechin type, and that in addition to the compounds previously enumerated, the so-called quebracho resin and guarana catechin are intermediate products of tannin formation. Again, according to Procter (private communication), a colourless catechin-like substance is to be found in mangrove cutch.

With the exception of coca-tannic acid, no crystalline catechol tannins have been described, but all are amorphous and very similar in appearance to natural gallotannin, although on keeping, especially in the moist condition, they are apt to develop a red tint. According to Perkin, most phlobatannins can be prepared in a nearly colourless condition by extracting a solution of the crude tannin to which sodium bicarbonate has been added with ethyl acetate (cf. *Gallotannin*).

Numerous phlobatannins have been isolated, and a description of them is given below, although it is extremely doubtful whether the majority of these are individuals. In many cases, indeed, the general reactions of these compounds are the same, and considering the extreme difficulty in the effective purification of amorphous preparations of this character, specific differences which have been observed will no doubt, on further investigation, largely disappear. Trimble (*loc. cit.*, ii., 132), who submitted certain phlobatannins to careful purification, found that there was a fair approximation in their percentage compositions, and it is thus natural to presume that the known members of this group are not so numerous as was formerly considered to be the case.

Anachueta wood and bark contain a tannin which gives a green coloration with iron salts.

Aspertannic acid, $C_{14}H_{16}O_8$, was obtained by Schwarz from Woodruff (*Asperula odorata*, Linn.), and gives a green colour with ferric salts. It does not yield precipitates with albumen, gelatin, and tartar emetic solutions.

Atherospermatannin, from the bark of *Atherosperma moschatum* (Labill.), gives a green colour with ferric salts. A lead salt,

$$C_{10}H_{14}PbO_3,$$

has been described by Zeyer (Jahrb. Min., 1861, 769).

Barbitamao tannic acid, from the bark of the *Stryphnodendron barbatimum* (Mart.), (Wilbuszwitcz, Ber. Ref., 1886, 19, 349), is an amorphous red powder, which yields a phlobaphene, and on fusion with alkali, *protocatechuic acid* and *phloroglucinol*.

Beech tannin, from the bark of the red beech, contains a tannin of the composition $C_{20}H_{22}O_9$ (Etti, Monatsh., 10, 650).

Caffetannic acid, $C_{15}H_{18}O_9$, occurs in coffee berries in the form of calcium and magnesium salts (Rochleder, Annalen, 59, 300); in cainia root, *Chiococca brachiata* (Ruiz. et Pav.), (Rochleder and Hlasiwetz, *ibid.*, 1848, 66, 35); *Nux vomica* (Sander, Arch. Pharm., 1897, 235, 133); St. Ignatius beans (*ibid.*), and Paraguay tea, *Ilex paraguensis* (A. St. Hill.), (Rochleder, Annalen, 1847, 66, 39), (cf. also Graham, Stenhouse and Campbell, J. pr. Chem., 1856, 69, 815; Arata, Ber., 1881, 14, 2251; Kunz-Krause, Arch. Pharm., 1893, 231, 613; Ber., 1897, 30, 1617).

It is an amorphous powder readily soluble in water, gives a dark-green coloration with ferric chloride, and when boiled with potassium hydroxide solution gives *caffeic acid* and a sugar (Hlasiwetz, Annalen, 1866, 142, 220), which is glucose (Sander, *loc. cit.*). On dry distillation *catechol* is formed, and by fusion with alkali *protocatechuic acid* is obtained. The ammoniacal solution becomes green on exposure to air with formation of *viridic acid*, a substance which is also present in coffee berries in the form of its calcium salt (Rochleder, Annalen, 63, 197). According to Griebel (Inaugural Diss. Munich, 1903) caffetannic acid is $C_{18}H_{24}O_{10}$, and a penta-acetyl derivative corresponding to this formula is described.

Callutannic acid, $C_{14}H_{14}O_9$, contained in heather, *Calluna vulgaris* (Salisb.), is an amber-coloured substance. It gives a green coloration with ferric chloride, and when heated with dilute mineral acids yields an amorphous anhydro derivative, $C_{14}H_{10}O_7$ (Rochleder, Annalen, 84, 354; Sitz. Ber., 9, 286).

Canaigre tannin is present in the tuberous roots of the *Rumex hymenosepalus* (Torr.), an important American tanning material. It has been submitted to an elaborate examination by Trimble ("The Tannins," 1894, ii., 115), who describes it as a yellowish-white powder readily soluble in water, which gives with lead acetate solution a yellow precipitate, and with ferric chloride a green precipitate. It reacts with bromine water to give a yellow deposit, and on heating to 160—190° is decomposed with production of *catechol*. Boiling 2 per cent. hydrochloric acid yields an insoluble red phlobaphene together with some *protocatechuic acid*. Sugar is not formed in this decomposition. Analysis gave C = 58·10; H = 5·33, figures

which approximate to, though they are somewhat lower than, those given by the best-known phlobatannins.

Catechutannic acid (see Catechu).

Cherry bark tannin, $C_{21}H_{20}O_{10} + \frac{1}{2}H_2O$, is present in the bark of the *Prunus cerasus* (Linn.), (Rochleder, Sitz. Ber., 59, 819), and gives a green coloration with ferric chloride. It is not a glucoside, but when digested with boiling dilute acids gives a red phlobaphene, $C_{21}H_{16}O_8 + \frac{3}{4}H_2O$.

Cocatannic acid, $C_{17}H_{22}O_{10} + 2H_2O$ (?), present in the leaves of the *Erythroxylon coca* (Linn.), (Niemann, Jahrb. Min., 1860, 386), is sparingly soluble in cold water and gives a green coloration with ferric salts. According to Warden (Pharm. J., 18, 985) it can be obtained in microscopic crystals of a sulphur yellow colour.

Colatannin or *Kolatannin*, $C_{16}H_{20}O_8$, a light red amorphous powder, exists in the Kola nut, *Cola acuminata* (Schott and Endl.), in combination probably with caffeine and theobromine (Knox and Prescott, Amer. Chem. J., 1897, 19, 63). With ferric acetate it gives a green coloration, and on fusion with alkali *protocatechuic acid* is obtained. *Penta-acetylkolatannin*, $C_{16}H_{15}O_8(C_2H_3O)_5$, colourless powder, *tribromkolatannin*, $C_{16}H_{17}O_8Br_3$, red-brown powder, *penta-acetyl-tribromkolatannin*, $C_{16}H_{12}O_8Br_3(C_2H_3O)_5$, *pentabrom*, and *hexabromkolatannin* have been described. On heating, kolatannin yields various anhydrides, $(C_{16}H_{19}O_7)_2O$ at 107—110°, $(C_{16}H_{17}O_6)_2O$ at 135—140°, and $C_{16}H_{16}O_6$ at 155—156°.

Cortepinitannic acid, $C_{32}H_{24}O_{17}$, occurs together with pinicortannic acid in the bark of the Scotch fir, *Pinus sylvestris* (Linn.). It consists of a bright red powder, the aqueous solution of which gives an intense green coloration with ferric chloride (Kawalier, Sitz. Ber., 11, 363).

Euphrasia tannin is present according to Enz (Vierteljahrsch. Pharm. J., 8, 175) in the green parts of *Euphrasia officinalis* (Linn.), and gives a green colour reaction with ferric salts. Its lead salt has the composition $C_{32}H_{20}Pb_3O_{20}$.

Fragarianin, v. *Strawberry tannin*.

Filitannic acid, $C_{41}H_{36}NO_{18}$ (?), exists in fern-root (*Aspidium filix mas*, Swartz.), (Malin, Annalen, 143, 276), and forms a red-brown powder which, in aqueous solution, gives an olive-green coloration with ferric chloride. By boiling with dilute sulphuric acid it gives *filix red*, $C_{20}H_{18}O_{12}$, an amorphous compound, and this when fused with alkali gives *phloroglucinol* and *protocatechuic acid* (cf. also Reich, Arch. Pharm., 1900, 238, 648).

Fraxitannic acid, $C_{36}H_{32}O_{14}$ (?) occurs in the leaves of the ash

tree, *Fraxinus excelsior* (Linn.). It consists of a brownish-yellow deliquescent powder, and when heated at 100° loses water and forms an almost insoluble anhydride, $C_{26}H_{30}O_{13}$ (Gintl and Reinitzer, Monatsh., 3, 745). Aqueous ferric chloride produces a dark green coloration, and when oxidised with permanganate this tannin yields quinone. *Acetylfraxitannic acid*, $C_{26}H_{28}O_{14}(C_2H_3O)_4$, *benzoylfraxitannic acid*, $C_{26}H_{28}O_{14}(C_7H_5O)_4$, *tribromfraxitannic acid*,

$$C_{26}H_{29}Br_3O_{14},$$

and *tetra-acetyltribromfraxitannic acid*, $C_{26}H_{25}Br_3O_{14}(C_2H_3O)_4$, have been described.

Galitannic acid, $C_{14}H_{16}O_{10}$, H_2O, exists in the bark of the *Galium verum* (Linn.), (Schwarz, Annalen, 83, 57). It gives a yellow precipitate with basic lead acetate and a green colour reaction with ferric chloride.

Guarana tannin is present in the *Paullinia cupana* (H. B. and K.), the seeds of which, known as "guarana," contain theine and are extensively used in South America for medicinal purposes. According to Nierenstein (Die Gerbstoffe, 20) the tannin consists of small colourless crystals, melting-point 199—201°, and yields an acetyl derivative, melting-point 134—136°. It is lævo-rotatory, having $[\alpha]_D^{20} = -72{\cdot}4°$ in water, and $[\alpha]_D^{20} = -39{\cdot}1°$ in alcohol.

Hemlock tannin, $C_{20}H_{18}O_{10}$ (?) is present in Hemlock bark, *Tsuga* [*Abies*] *canadensis* (Carr.), the extract of which is prepared on a very large scale in North America for tanning purposes. According to Böttinger (Ber., 1884, 17, 1125), it is probably related to the quercitannic acid of the oak, and on heating with sulphuric or hydrochloric acid gives the anhydride *hemlock red*, $C_{40}H_{30}O_{17}$. With hydrochloric acid at 180°, hemlock red evolves methyl chloride; when heated with acetic anhydride the acetyl compound

$$C_{40}H_{23}O_{17}, (C_2H_3O)_7$$

is produced, whereas bromine gives a mixture of the compounds $C_{40}H_{30}Br_{10}O_{17}$ and $C_{40}H_{16}Br_{14}O_{17}$. Bromine added to the diluted tannin extract precipitates *tetrabromhemlock tannin*, $C_{20}H_{14}Br_4O_{10}$, a yellow powder which yields the *penta-acetyl* derivative

$$C_{20}H_9Br_4O_{10}(C_2H_3O)_5,$$

and by the further action of bromine the bromine compound

$$C_{20}H_{12}Br_6O_{10}$$

(*cf.* Trimble, Amer. J. Pharm., 1897, 69, 354, 406; J. Soc. Chem. Ind., 1898, 17, 558) is produced.

Hop tannin, $C_{22}H_{26}O_9$, present in hops (*Humulus lupulus*, Linn.), (Etti, Annalen, 180, 223; Monatsh., 10, 651), has all the properties of a catechol tannin. It gives with ferric chloride a dark green coloration and with boiling dilute mineral acid the phlobaphene "hop red," $C_{22}H_{26}O_{15}$. Hop red forms a cinnamon-coloured powder and on fusion with potash yields *phloroglucinol* and *protocatechuic acid*.

Horse chestnut tannin, $C_{26}H_{24}O_{12}$, is present in nearly all parts of the *Aesculus hippocastanum* (Linn.) and in the root bark of the apple tree (Rochleder, Sitz. Ber., 53, [ii.], 478; 54, [ii.], 609). It consists of a nearly colourless powder, the solution of which gives a green coloration with ferric chloride, and when boiled with dilute mineral acid the phlobaphene $C_{26}H_{22}O_{11}$ or $C_{26}H_{20}O_{10}$. On fusion with alkali, *phloroglucinol* and *protocatechuic acid* are produced. *V.* also *phyllæscitannin* and CHESTNUT EXTRACT.

Ipecacuanhic acid, $C_{14}H_{18}O_7$, was obtained by Willigt (Annalen, 76, 345) from the roots of *Psychotria ipecacuanha* (Stokes), and consists of a reddish-brown, bitter hygroscopic substance. Its solution gives a green coloration with ferric chloride.

Japonic acid (see CATECHU).

Kino (see KINO).

Larch tannin.—The bark of the larch, *Larix europaea* (DC.), contains considerable quantities of a tannin which was examined by Stenhouse (Phil. Mag., 23, 336). It forms an olive-green precipitate with ferric salts, and when boiled with dilute sulphuric acid a red phlobaphene is produced.

Maletto tannin occurs in the bark of *Eucalyptus occidentalis* (Endl.) and other species of eucalyptus. According to Strauss and Geschwender (Zeitsch. angew. Chem., 1906, 19, 1121) it possesses the formula $(C_{42}H_{50}O_{20})_2$, and appears to be identical with quebracho tannin. Dekker (Arch. Néerland., 1909, ii., 14, 50) prefers the formula $(C_{19}H_{20}O_9)_m$, and describes the acetyl derivative

$$C_{38}H_{28}O_{17}Ac_{10}$$

and benzoyl derivative $C_{19}H_{25}O_{12}Bz_5$. Heated with zinc-dust and sodium hydroxide solution the tannin gives small quantities of *gallic acid* and *phloroglucinol*, whereas dry distillation yields *pyrogallol* and traces of other phenols. Boiling dilute sulphuric acid forms "maletto red," $C_{57}H_{50}O_{22}$, from which the *acetyl* derivative

$$C_{57}H_{38}O_{22}Ac_{16}$$

can be obtained.

Mangrove tannin, $C_{24}H_{26}O_{13}$.—This important tannin is derived from the *Rhizophora mangle* (Linn.), *R. mucronata* (Lam.), *Ceriops candolleana* (Arn.), *C. roxburghiana* (Arn.), and other allied species. It is described as an amorphous red powder, which on fusion with alkali gives *protocatechuic acid*, and with boiling dilute sulphuric acid the phlobaphene $C_{48}H_{46}O_{21}$. The *monacetyl* derivative

$$C_{24}H_{25}O_{12}(C_2H_3O)$$

melts at 205° (Nierenstein, Die Gerbstoffe). This tannin closely resembles in its properties catechutannic acid (see CATECHU), and indeed mangrove cutch and catechu may be employed in many cases for the same purpose. Possibly these two substances are identical, and Procter (private communication) has isolated from mangrove cutch a small quantity of a colourless crystalline substance resembling catechin. Perkin who examined an ethyl acetate extract of the fresh bark of the *C. candolleana*, prepared in Borneo, was unable to detect the presence of a catechin, but obtained the tannin as a pale yellow powder, which gave a green coloration with ferric chloride solution, and resembled catechutannic acid in many respects.

Mimosa tannin is derived from various species of *Mimoseae*, such as the *Acacia arabica* (Willd.) of Egypt, the so-called "Wattles" of Australia, and numerous others. The tannin present is interesting in that though it possesses the reactions of a phlobatannin, such as phlobaphene production, precipitation by bromine water and solubility of its lead compound in acetic acid, etc., it gives a bluish-violet coloration with ferric chloride. Ammonium sulphide gives a precipitate with a mimosa solution, when after removal of the excess by boiling, a few drops of sulphuric acid are added, followed by a small quantity of salt. All other phlobatannins, except Maletto and Pistaschia tannins, give no precipitate by this method (Stiansy, private communication).

Moritannic acid, see *Maclurin*.

Oxypinitannic acid, v. *Pinitannic acid*.

Oak bark tannin or *Quercitannic acid* is found in the bark of the oak, and is not to be confused with the tannin of oak-wood from which it is distinct, and which is described below under the name of quercinic acid. In 1792 George Swayne communicated to the Society of Arts his results on the use of oak leaves in tanning (Trimble, "The Tannins," ii., 51), and the subject was again discussed by Berzelius in his Lehrbuch, 1827, and by Liebig (Handbuch der Chemie, 1843). Assumed at that time to be identical with the tannin of nut-galls (gallotannin), it was first shown by Stenhouse

(Phil. Mag., 22, 425) to differ from this substance. According to Grabowski (Sitz. Ber., 56, [ii.], 388), Oser (*ibid.*, 72, [ii.], 178), Johanson (Arch. Pharm., [iii.], 9, 210), Böttinger (Ber., 14, 1598), quercitannic acid is in reality a glucoside, but Etti (Ber., 14, 1826; Monatsh., 4, 512) found that the pure substance did not yield a trace of sugar. Various formulæ have been assigned to this substance, viz. Eckert (Jahres., 1864, 608), $C_{28}H_{20}O_{20}$; Oser (Jahres., 1875, 600), $C_{20}H_{20}O_{11}$; Löwe (Zeitsch. anal. Chem., 20, 210), $C_{28}H_{30}O_{15}$; Böttinger (Ber., 1883, 16, 2712), $C_{15}H_{12}O_9$, $2H_2O$, and Etti (Monatsh., 10, 650), $C_{17}H_{16}O_9$, $C_{18}H_{18}O_9$, and $C_{20}H_{20}O_9$.

Quercitannic acid is described by Etti as a reddish-white powder almost insoluble in water. One of its most characteristic properties is the readiness with which it forms reddish-brown anhydrides when heated by itself or with dilute acids. Thus at 130—140° the *first anhydride*, $C_{34}H_{30}O_{17}$, is produced, and this by heating with dilute sulphuric or hydrochloric acid gives the *second anhydride*, $C_{34}H_{28}O_{16}$. Boiling dilute sulphuric acid again converts the original tannin into the *third anhydride*, $2C_{17}H_{16}O_9 - 3H_2O = C_{34}H_{26}O_{15}$.

These compounds are insoluble in water, but colour a solution of ferric chloride blue (?). Löwe (*loc. cit.*) again examined an anhydride, $C_{28}H_{24}O_{12}$, and an "oak red," $C_{28}H_{22}O_{11}$. Böttinger, who prepared the oak red from the tannin by means of dilute sulphuric acid, adopted the formula $(C_{14}H_{10}O_6)_2$, H_2O. Etti (Ber., 1884, 17, 1823) isolated from the bark of the *Quercus pubescens* (Willd.) a tannin $C_{20}H_{20}O_9$, practically identical with the substance $C_{17}H_{16}O_9$ previously found in the *Q. robur* (Linn.), but giving a green solution with ferric chloride, and not a blue, as formerly stated.

When heated with dilute sulphuric acid at 130—140°, quercitannic acid gives in addition to anyhydride 1·5 per cent. of *gallic acid*, and with strong hydrochloric acid at 150—180° the formation of oak red was accompanied by the evolution of methyl chloride (Etti, Monatsh., 1, 274). On dry distillation it yields *dimethylcatechol* and *catechol*, and on fusion with alkali *protocatechuic acid*, *catechol*, and *phloroglucinol*.

By the action of bromine on the aqueous bark extract, Böttinger (Ber., 1883, 16, 2710) obtained *dibromquercitannic acid*, $C_{19}H_{14}Br_2O_{10}$, as a yellow precipitate, and from this *penta-acetyldibromquercitannic acid* was prepared. Heated with hydrochloric acid at 180°, *methyl chloride* was evolved, and by means of hydroxylamine hydrochloride the compound $C_{19}H_{15}Br_2NO_{10}$ was produced. Reduced with sodium amalgam *hydroquercinic acid*, $C_{15}H_{18}O_7$ or $C_{15}H_{16}O_6$, and *hydroquergalic acid*, $C_{14}H_{14}O_6$, are formed (Annalen, 263, 121). When

suspended in chloroform and further brominated it yields *tetrabromdehydroquercitannic acid.* Quercitannic acid was thus $C_{19}H_{16}O_{10}$, contained five hydroxyls, and the group $COCH_3$.

According to Etti (Monatsh., 10, 647) a further investigation of the tannins $C_{17}H_{16}O_9$ and $C_{20}H_{20}O_9$ has proved that they are not glucosides, but derivatives of a ketone acid,

$$C_6H_2(OH)_3 . CO . C_6H(OH)_2COOH$$

Trimble ("The Tannins," 1894, ii., 77) carried out an elaborate investigation of the tannins present in the barks of the *Quercus alba* (Linn.), *Q. coccinea* (Wangenh.), *Q. discolor* (Ait.), *Q. falcata* (Michx.), *Q. palustris* (Du Roi), *Q. prinus* (Linn.), *Q. bicolor* (Willd.), *Q. obtusiloba* (Michx.), *Q. phellos* (Linn.), *Q. rubra* (Linn.), *Q. robur* (Linn.), *Q. semicarpifolia* (Sm.), employing acetone for the purpose of extraction. The tannins in most cases had a pale yellow colour, gave with ferric chloride a *green* coloration, and practically identical results with all the usual tannin reagents.

Heated with glycerol at 160°, the tannins of *Q. tinctoria*, *Q. palustris*, *Q. falcata*, and *Q. phellos* yielded *catechol*, whereas with fused alkali the eight samples examined gave *protocatechuic acid.* Though all these compounds produce a violet colour on pine wood moistened with hydrochloric acid, phloroglucinol or other phenol was not detected among their decomposition products. Heated with 2 per cent. hydrochloric acid for two and a half hours, a phlobaphene separated, whereas the solution contained protocatechuic acid. Analyses of nine of these tannin preparations showed but little variation, the average being C = 59·79; H = 5·08, and approximately correspond with those of Etti (*loc. cit.*) for the tannin $C_{20}H_{20}O_9$ from *Q. pubescens*, and of Kraemer (Amer. J. Pharm., 1890, 236) for the tannin of *Q. alba.*

Oak wood tannin, Quercin, Quercic acid, Quercinic acid, $C_{15}H_{12}O_9$, $2H_2O$, consists of a light brownish-yellow substance, and is distinguished from the quercitannic acid of oak bark in that its aqueous solution gives a blue, not green, coloration with ferric chloride, and does not yield a precipitate with bromine water (Böttinger, Ber., 1887, 20, 761).

With the object of isolating the tannin in a pure condition, Böttinger acetylated a purified extract of the wood, and decomposed the acetyl compound $C_{15}H_7(C_2H_3O)_5O_9$ by heating it with water at 135°. By the action of sodium amalgam on the acetyl derivative, Böttinger (Annalen, 263, 110) obtained *hydroquercic acid*, $C_{15}H_{18}O_7$

or $C_{15}H_{16}O_6$, *querlactone*, $C_5H_6O_2$, and an acid which is probably trihydroxybutyric acid.

Hydroquercic acid is a grey-brown, bitter hygroscopic powder, which forms the *acetyl* derivative $C_{15}H_{14}(C_2H_3O)_2O_6$, the *barium* salt $(C_{15}H_{15}O_6)_2Ba$, and the *lead* salt $(C_{15}H_{15}O_6)_2Pb$. Querlactone, on the other hand, forms the salt $(C_5H_7O_3)_2Pb$. As above noted, hydroquercinic acid could also be obtained in a similar manner from quercitannic acid.

Etti (Monatsh., 10, 647) isolated from the wood of the Slavonian oak a tannin $C_{16}H_{14}O_9$ which appeared to be a ketonic compound. This is present in the wood in the form of a readily soluble salt (probably magnesium salt). Crystallised from alcohol, it forms brownish-red microscopic warty spherical masses, insoluble in water, and having the properties of a monobasic acid (*cf.* Fuchs, Monatsh., 9, 1132). With phenylhydrazine it gives the compound $C_{22}H_{20}N_2O_8$, forms a brown amorphous oxime $C_{16}H_{15}NO_9$, and with dilute sulphuric acid at 120—130° yields *gallic acid* in addition to a red anhydride. Heated alone at 130—135°, or in a sealed tube with water at 100°, anhydrides are also produced, which on boiling with hydriodic acid evolve methyl iodide. On long digestion of the tannin $C_{16}H_{14}O_9$ with hydrochloric acid at 100°, a methoxyl group is split off, with production of a yellow coloured acid $C_{15}H_{12}O_9$ in which a methoxyl group is still present. This tannin is therefore probably the dimethyl ether of the ketonic acid formulated above.

On boiling the tannin with dilute sulphuric acid, the anhydride $C_{32}H_{24}O_{16}$ is produced, whilst on heating in a closed tube the anhydrides $C_{32}H_{20}O_{14}$ and $C_{32}H_{18}O_{13}$ were obtained.

The varied results of many of these workers with the oak tannins appear to be due, as suggested by Trimble, to the fact that in many cases they employed oak tannin extracts of doubtful authenticity. Thus it is possible that Etti, who in his earlier work describes the tannin as producing a blue coloration with ferric chloride, was in reality examining oak-wood and not oak-bark preparations, and again the peculiar insoluble property of certain of his tannins, also commented on by Trimble, suggests that in these cases he investigated an anhydride rather than the tannin itself. That oak barks contain a phlobatannin possessing a catechol nucleus appears to be certain from the investigations of Trimble, and it seems probable that in the wood either a pyrogallol tannin or a phlobatannin containing a pyrogallol group is present. Though, as stated above by Etti in the case of the Slavonian oak, this yields phlobaphenes, Stiasny (private communication) considers that such is not usually the property of

oak-wood extracts. An interesting point, moreover, apparently not stated in the literature, though well known to tanners, is that oak-wood extracts give some ellagic acid, and on this account impart to leather the "bloom" so characteristic of this substance.

Oenotannin, $C_{19}H_{16}O_{10}$ (?), was obtained by Gautier from red wine (Bull. Soc. chim., 1877, 27, 496), who describes it as a colourless substance readily soluble in water. It gives a green coloration with ferric chloride solution, by fusion with alkali *protocatechuic acid* and *phloroglucin*, and when exposed to moist air becomes converted into an insoluble red phlobaphene-like substance. According to Heise (Ber. Ref., 22, 823), oenotannin contains gallotannin and is a mixture of three compounds.

Pistachia tannin is present in the leaves of the *Pistacia lentiscus* (Linn.) in addition to some quantity of a gallotannin (Perkin and Wood, Chem. Soc. Trans., 1898, 73, 378), and consists of a pale brown brittle mass which with iron alum solution gives a blue-black coloration. With boiling dilute sulphuric acid a phlobaphene quickly separates, and when fused with alkali, *gallic acid* and *phloroglucinol* are produced.

Phyllæscitannin is the name given by Rochleder to a tannin present in the small leaflets of the horse chestnut, as long as they remain enclosed in the buds (Zeitsch. für Chem., 1867, 84). It is described as an amorphous red-brown substance of the formula $C_{26}H_{24}O_{13}$, H_2O, having a strongly astringent taste.

Pinicortannic acid and *cortepinitannic acid* occur in the bark of the Scotch fir, *Pinus sylvestris* (Linn.), and can be separated owing to the fact that in aqueous solution the former only is precipitated by means of lead acetate. Pinicortannic acid forms a reddish-brown powder of the composition $(C_{16}H_{18}O_{11})_2$, H_2O, which after drying is sparingly soluble in water. It gives a green coloration with ferric chloride, and when boiled with dilute acids gives the phlobaphene $C_{48}H_{50}O_{21}$ (Kawalier, Sitz. Ber., 11, 361).

Pinitannic acid and *oxypinitannic acid* occur in the needles of the Scotch fir, *Pinus sylvestris* (Kawalier), and are distinguished from one another by the fact that the former only is precipitated by lead acetate solution. *Pinitannic acid*, according to Rochleder (Sitz. Ber., 29, 60), also present in the *Thuja occidentalis*, is a reddish-yellow substance which gives a red-brown coloration with ferric chloride and when boiled with dilute acids a sparingly soluble red product (phlobaphene).

Oxypinitannic acid, on the other hand, yields a green solution with ferric chloride (Kawalier).

Quebracho tannin or *Quebrachitannic acid*, see QUEBRACHO COLORADO.

Quinotannic acid or *Cinchonatannic acid* obtained from cinchona bark is a light yellow very hygroscopic substance, a solution of which gives a green precipitate with ferric salts. On digestion with boiling dilute sulphuric acid, it is converted into a sugar and cinchona red $C_{28}H_{22}O_{14}$ (Rembold, Annalen, 143, 270), and from the latter by fusion with alkali, *protocatechuic* and acetic acids are produced (Hlasiwetz, *ibid.*, 143, 307). According to Schwarz (Sitz. Ber., 7, 250), quinotannic acid has the composition $C_{14}H_{16}O_9$, whereas cinchona red is to be represented as $C_{12}H_{14}O_9$.

Quinovatannic acid, contained in the bark of the *Cinchona nova*, in many respects resembles quinotannic acid (Hlasiwetz, Annalen, 79, 129). With ferric chloride it gives a dark green coloration, and with boiling dilute acids quinova red $C_{12}H_{12}O_5$ is produced. On fusion with potash it yields *protocatechuic acid*.

Rhamnotannic acid (so-called), present in buckthorn berries, is in reality not a tannin matter.

Rhatany tannin, $C_{20}H_{20}O_9$, from the bark of rhatany root. *Krameria triandra* (Ruis and Pav.), (Willstein, Jahres., 1854, 656) is described by Raabe (*ibid.*, 1880, 1060) as a light yellow powder, readily soluble in water. Its solution gives with ferric chloride a green coloration. When heated with dilute acids it yields rhatany red, $C_{22}H_{22}O_{11}$, and a sugar (Grabowski, Annalen, 143, 274), whereas according to Raabe (*loc. cit.*) no sugar is thus produced and the red substance possesses the composition $C_{20}H_{18}O_9$. By dry distillation rhatany red yields catechol, and *protocatechuic acid* and *phloroglucinol* when fused with alkali.

Rheotannic acid or *Rhubarb tannic acid*, $C_{26}H_{26}O_{14}$, derived from rhubarb, forms a yellowish-brown readily soluble powder, the solution of which gives with ferric chloride a black-green precipitate. With boiling dilute acids it gives *rheic acid* (rheumic acid), $C_{20}H_{16}O_9$, and a fermentable sugar (Kubly, Zeitsch. für Chem., 1868, 308), although according to Tschirch and Neuberger (Schweiz, Wochenschr. Chem. Pharm., 1902, 282) in this manner *rheum-red*, $C_{40}H_{32}O_{18}$, *cinnamic acid*, *gallic acid*, and sugar are produced. According to Gilson (Chem. Zentr., 1903, i., 722, 882), two glucosides are present, *glucogallin*, $C_{13}H_{16}O_{10}$, giving gallic acid and dextrose, and *tetrarin*, $C_{32}H_{32}O_{10}$, from which *rheosurin*, $C_{10}H_{12}O_2$, *cinnamic acid*, and *gallic acid* can be produced. According to Krembs (Inaugural Diss., 1903, Berne), a catechin is also present in rhubarb.

Rhodotannic acid, $4C_{14}H_{12}O_7$, $3H_2O$, found in the leaves of *Rhodo-*

dendron ferrugineum (Linn.), is an amber-coloured substance which gives a green coloration with ferric chloride solution. Heated with dilute mineral acids, a reddish-yellow precipitate of *Rhodoxanthin*, $C_{14}H_{14}O_8$, is produced (Schwarz, Sitz. Ber., 9, 298).

Rubinic acid, v. CATECHU.

Rubitannic acid, $2C_{14}H_{22}O_{12} + H_2O$, was obtained by Willigt (Annalen, 82, 340) from the leaves of *Rubia tinctorium* (Linn.). It gives a green colour reaction with ferric chloride.

Sequiatannic acid, $C_{21}H_{20}O_{10}$, was isolated from the cones of *Sequoia gigantea* (Torr), (California), by Heyl (Pharm. Zentr., 1901, 42, 379) as a reddish-brown powder, soluble in water and yielding the salts $MgC_{21}H_{18}O_{10}$ and $CaC_{21}H_{18}O_{10}$. Boiled with dilute sulphuric acid, a phlobaphene, *gallic acid*, and a sugar are produced. The *hexa-acetyl*, $C_{21}H_{14}O_{10}(C_2H_3O)_6$, *hexabenzoyl*, $C_{21}H_{14}O_{10}(C_7H_5O)_6$, and *bromine*, $C_{21}H_{15}O_{10}Br_5$, derivatives of this tannin are amorphous.

Sorbitannic acid, from the juice of the ripe berries of the mountain ash, *Sorbus aucuparia* (Linn.), forms a thick syrupy mass, which gives a green coloration with ferric chloride solution. It yields *catechol* on dry distillation, and *protocatechuic acid* and *phloroglucinol* when fused with alkali (Vincent and Delachanal, Bull. Soc. chim., [ii.], 47, 492).

Spruce-bark tannin, $C_{21}H_{20}O_{10}$ (?) gives, according to Böttinger, an unstable bromo derivative $C_{21}H_{14}Br_6O_{10}$. This reacts with hydroxylamine hydrochloride, and with hydrochloric acid at 180—190° evolves *methyl chloride*. The *penta-acetylpentabromo* derivative

$$C_{21}H_{10}Br_5O_{10}(C_2H_3O)_5$$

was also prepared. With boiling dilute hydrochloric acid the tannin yields *spruce red* which gives the acetyl derivative

$$C_{42}H_{27}(C_2H_3O)_7O_{17},$$

and when suspended in chloroform and treated with bromine the compound $C_{42}H_{24}Br_{10}O_{17}$ (Böttinger, Ber., 17, 1127).

Strawberry-root contains a tannin *fragarianin* (Phipson, Jahres., 1878, 891), the solution of which gives a green colour with ferric chloride. Boiling dilute hydrochloric acid forms *glucose* and a red substance *fragiarin*. On dry distillation the tannin gives traces of *catechol*, and when fused with alkali *protocatechuic acid* is produced.

Tannecortepinic acid, $C_{28}H_{26}O_{12}$, according to Rochleder and Kawalier (Sitz. Ber., 29, 23), can be isolated from the bark of young Scotch firs collected in the spring time. Ferric chloride gives a green coloration and boiling dilute acid a phlobaphene in addition to a little sugar.

Tannopinic acid, $C_{28}H_{30}O_{13}$ (?) is sometimes present in the needles of the Scotch fir gathered in the spring (Rochleder and Kawalier). In the winter time, oxypinitannic acid (*loc. cit.*) appears to take its place.

Tea tannin is probably identical with the quercitannic acid of oak bark (Stenhouse, Phil. Mag., 23, 332; Rochleder, Annalen, 63, 205; and Hlasiwetz and Malin, J. pr. Chem., [i.], 101, 109).

Tormentilla tannin, $C_{26}H_{22}O_{11}$, from the root of *Potentilla tormentilla* (Neck.), is an amorphous reddish powder, which colours ferric chloride solution blue-green. Boiled with dilute acids it produces *tormentil-red* without appreciable formation of sugar, and this appears to have the same composition as the tannin itself. With fused alkali *phloroglucinol* and *protocatechuic acid* are obtained. The root also contains a substance which yields *ellagic acid* when boiled with potash solution (Rembold, Annalen, 145, 5).

Viridic acid, $C_{14}H_{20}O_{11}$ (?), which exists in coffee beans as a calcium salt (Rochleder, Annalen, 63, 197), is obtained by the air oxidation of an ammoniacal solution of caffetannic acid, and forms a brown amorphous mass, the alkaline solutions of which are green. The salts, $Ba_2C_{14}H_{16}O_{11}$, $PbC_{14}H_{12}O_8$, and $PbC_{14}H_{14}O_9$, have been described (*cf.* also Vlaanderen and Mulder, Jahres., 1858, 261).

Willow bark tannin.—The bark of *Salix triandra* (Linn.) contains a glucoside tannin which gives a green colour reaction with ferric chloride, and when boiled with dilute sulphuric acid a brown-red precipitate (Stenhouse, Proc. Roy. Soc., 11, 403; Johanson, Arch. Pharm., [iii.], 13, 103).

Tannins are frequently accompanied in the plant by yellow colouring matters, and it has been pointed out by Perkin that a relationship is usually to be observed between these compounds in respect of the phenolic nuclei present in each. Thus catechu contains catechutannic acid and quercetin, both of which contain phloroglucinol and catechol groups, whereas both the cyanomaclurin and morin of Jakwood (*Artocarpus integrifolia*, Linn.) yield phloroglucinol and β-resorcylic acid. Again, in sumach (*R. coriaria*, Linn.), *Pistacia lentiscus*, Linn. (leaves) and *Hæmatoxylon campeachianum*, Linn. (leaves), a gallotannin and myricetin exist, both of which are pyrogallol derivatives.

Other similar instances of this relationship could be cited; and where a divergence of this rule at first sight seems evident, this is frequently more apparent than real, as in the case of Young Fustic (*R. cotinus*, Linn.), which is known to contain a gallotannin and fisetin (catechol and phloroglucinol). From the reactions of the wood extract, however, catechol tannin must also be present.

Gall-nuts.

These are morbid excrescences produced by the puncture of an insect called *Cynips gallæ-tinctoriæ* upon the leaves and young twigs of certain kinds of oak trees, more especially those of *Quercus infectoria* (Oliver), *Q. lusitanica* (Lam.), growing in the East Indies, Persia, the Levant. If the fully developed nut be broken open it will be seen to contain a central cavity, in which the larva of the insect will be found. As a rule the galls are collected before the larvæ are fully developed, and therefore before they have perforated the galls and escaped as mature insects. In this condition they contain the most tannic acid and are known as *blue*, *black*, or *true nuts*. The less valuable or perforated variety are larger and paler in colour and are known as *white* or *false nuts*.

Aleppo galls are one of the best varieties on the market, and should contain from 50—60 per cent. of tannic acid. This same oak, the *Quercus infectoria*, also bears a large gall known as the Apple of Sodom, due to a different insect, which contains from 24—34 per cent. of tannin and has been used for tanning purposes.

Other varieties are Smyrna galls, Austrian, and Hungarian galls, and of these the former are considered best. English oaks yield several species of galls and oak apples, which, however, are not of much value.

Chinese galls are produced by the action of an insect termed the *Aphis chinensis* on a species of sumach, *Rhus semilata*. These are hollow and possess very thin walls, but are much larger and more irregular in shape than the ordinary Aleppo variety, moreover, when freshly gathered, they are covered with a very fine down. They are much esteemed owing to their richness in tannin matter, of which frequently as much as 70 per cent. is present. On this account they are largely employed for the manufacture of *tannic acid*.

Gall-nut extract is employed for mordanting purposes when very delicate shades are required. In addition to tannic acid, all varieties of gall-nuts appear to contain minute traces of ellagitannic acid.

Chestnut Extract.

The wood of the Spanish chestnut, *Castanea vesca*, though it contains only 3—6 per cent. of tannin, is the source of the much-valued chestnut extract. The bark contains more tannin than the wood (17 per cent.), but is not much used. The tree, which grows to from 60 to 80 feet in height, is abundant in Italy, the South of France,

and Corsica, where it forms immense forests, and it is also very common in America.

Trimble ("The Tannins"), who very carefully examined the tannin, obtained analytical data and reactions which indicated that it was identical, or nearly so, with gallotannin, but it is probable that this wood also contains traces of a catechol tannin, for a certain quantity of a red colouring matter is also present, which resembles in character a phlobaphene. Some writers have suggested that chestnut tannin is a methyl ether of ordinary gallotannin, but there is apparently no definite evidence in support of this theory.

Chestnut is employed almost entirely in the form of extract, the strength of which varies, but usually contains from 26 to 32 per cent. of tannin. The extract is frequently decolorised, and some times mixed with quebracho extract and other materials. Chestnut tannin is the tannin which is most largely employed for the dyeing of silk. *Castanea vesca* appears to be frequently confused with the horse-chestnut, *Æsculus hippocastanum*. The tannin derived from this latter is, however, of little or no practical value.

SUMACH.

True sumach consists of the dried and usually powdered leaves of the genus *Rhus* (order *Terebinthaceæ*), and is useful for tanning the finer kinds of leather, and also in dyeing and calico printing on account of the tannin matter present in it.

Sicilian sumach, the variety most esteemed in this country and throughout Europe, consists of the leaves of the *Rhus coriaria* (Linn.), a shrubby bush cultivated to a large extent in Sicily, where the sumach industry is of considerable importance. When the plant is about to flower the younger twigs are removed, dried in the sun, and subsequently beaten to remove the leaves and flower panicles. The sumach is imported sometimes in leaves, but more often in the form of powder, and should contain about 25 per cent. of tannin, although as much as from 27—32 per cent. may occasionally be found.

According to Löwe (Zeitsch. anal. Chem., 12, 128), the tannin matter present, $C_{14}H_{10}O_9$, is ordinary gallotannin; indeed it is well known that when an aqueous extract of the sumach is boiled with dilute sulphuric acid, considerable quantities of gallic acid are produced. On the other hand, Strauss and Geschwender (Zeitsch. angew. Chem., 1906, 1121), who isolated the tannin according to Löwe's instructions, detected the presence of a methoxy group, and suggest the formula $C_{32}H_{29}O_{11}$. OMe.

Sicilian sumach contains also a trace of an ellagitannin and

myricetin, $C_{15}H_{10}O_8$, to the extent of about 0·1173 per cent. (Perkin and Allen, Chem. Soc. Trans., 1896, 69, 1299), the latter colouring matter having been previously mistaken by Löwe (Zeitsch. anal. Chem., 1874, 12, 127) for quercetin.

Considerable quantities of sand and sometimes particles of magnetic iron ore, which cause black stains, are often to be found in sumach (Procter, "Principles of Leather Manufacture," 1903, 271); (compare also Trotman, J. Soc. Chem. Ind., 1904); and it is frequently highly adulterated in the ground condition with the leaves and twigs of various plants. Of these, the *Pistacia lentiscus* (Linn.) ("schinia" or "skeñs"), *Coriaria myrtifolia* (Linn.), (French sumach or "stinco"), *Tamarix africana* (Poir.) (brusca), *Tamarix gallica* (Linn.), *Ailanthus glandulosa* (Desf.), *Ficus carica* (Linn.), *Vitis vinifera* (Linn.), other species of the Rhus family and also the ground branches ("gambuzza," "gammuzza") of the *Rhus coriaria* itself, are known to be employed. These sumach adulterants also contain tannin matters, but for tanning and dyeing purposes are as a rule much inferior to sumach itself.

The *Pistacia lentiscus* (Linn.), (mastic tree), a small tree about 20 feet high with evergreen leaves, grows abundantly in Cyprus. The leaves of this plant constitute the most important sumach adulterant, and about 10,000 tons are said to be exported from Tunis to Sicily annually and re-exported thence (as sumach?). According to Procter (*loc. cit.*) the leaves contain 12—19 per cent. of a catechol tannin. A good plump leather can be obtained from this material, but of a faintly reddish tint, the result being intermediate in character between those which are given by oak bark and sumach. Its presence in sumach is to be deprecated, and in many cases leads to injurious results. A considerable quantity, however, is consumed at Lyons in France as an assistant dyeing material for silk stuffs.

According to Perkin and Wood (Chem. Soc. Trans., 1898, 73, 374), these leaves contain a tannin closely allied to, if not identical with, ordinary gallotannic acid, as when an aqueous extract is boiled with dilute sulphuric acid a considerable quantity of gallic acid is produced. A second tannin or tannin glucoside is also present which, although possessing the general characteristics of the so-called "catechol" tannins in that it yields a red phlobaphene, and as noted by Procter, a reddish-coloured leather, gives, by fusion with alkali, *gallic acid* and *phloroglucinol*.

In addition to these tannins, myricetin (probably as glucoside) $C_{15}H_{10}O_8$ is also present to the extent of about 0·15 per cent.

Tamarix africana (Poir.) is a small shrub or tree characterised by its twiggy branches and minute scale-like leaves. The small twigs are collected in Tunis and imported into Sicily for the adulteration of sumach (Procter).

According to Perkin and Wood (*loc. cit.*) the leaves contain a tannin probably identical with gallotannin, in addition to a small quantity of an ellagitannin. A trace of yellow colouring matter is also present and consists of a *quercetin methylether*, $C_{16}H_{12}O_7$.

The *Tamarix gallica* (Linn.) closely resembles in appearance the *Tamarix africana* and flourishes in Cyprus, where the latter is not found. According to Procter, it contains 8·4 per cent. of tannin matter.

Ailanthus glandulosa (Desf.) is a tree of large size and handsome appearance, native of India and China, but common on the Continent. The leaves contain 11·2 per cent. of tannin matter (Procter), and this resembles gallotannin, although a trace of an ellagitannin is also present (Perkin and Wood). Curiously enough, although so high a percentage of tannin is present, leather is scarcely tanned by an extract of these leaves, but is merely stained a dull dirty colour. This material is therefore of little use for tanning purposes, and as an adulterant of sumach exerts a deleterious influence. A small quantity of quercetin can be isolated from the leaves.

The leaves of the *Ficus carica* (Linn.) (common fig tree) contain 1·6 per cent. of tannin (Procter) and a trace of a yellow colouring matter (Perkin and Wood). Skin is untanned by an extract of these leaves, but acquires, during the process, a dirty olive tint.

Gambusza consists of the small stalks branching from the main root of the *Rhus coriaria* (Linn.), which are ground to powder and mixed with sumach. The material contains some quantity of a tannin resembling gallotannin, together with a trace of myricetin.

Attempts to detect the presence of these adulterants in sumach by chemical methods have not given satisfactory results, but should a prolonged boiling of the extract with dilute sulphuric acid cause the gradual precipitation of phlobaphene, the presence of the leaves of the *Pistacia lentiscus* may be suspected.

More satisfactory results can be obtained by microscopical examination, and an elaborate work on this subject has been carried out by Andreasch ("Sicilianischer Sumach und seiner Verfälschung," Wien, 1898); the book, however, is unsuitable for abstraction. A useful method, now generally adopted by leather trades chemists, has been devised by Lamb and Harrison (J. Soc. Dyers, 1899, 14, 60), and is based upon the behaviour of the leaf mixture with warm

nitric acid. Under such treatment, the more delicate leaf structure of sumach itself is completely destroyed, whereas the strong cuticles of *Pistachia lentiscus*, *Coriaria myrtifolia*, *Tamarix africana*, and *Ailanthus glandulosa* are unaffected and can then be readily recognised (compare also Lamb, *ibid.*, 1904, 20, 265). Again, the leaves of the *R. coriaria* are very easily distinguished from those of other plants employed for their adulteration, in that both upper and lower cuticles are covered with a dense growth of hairs (Priestman, J. Soc. Chem. Ind., 1905, 24, 231).

Venetian sumach or *Turkish sumach* consists of the leaves of the *Rhus cotinus* (Linn.), a small tree, the wood of which constitutes the yellow dyestuff known as "Young Fustic". The material contains about 17 per cent. of tannin, which resembles ordinary gallotannin, together with a trace of an ellagitannin. The presence of myricetin, $C_{15}H_4O_2(OH)_6$, in these leaves is interesting, in view of the fact that in the wood itself, fisetin, $C_{15}H_6O_2(OH)_4$, is present (Perkin, Chem. Soc. Trans., 1898, 73, 1016).

American sumach.—The leaves of numerous varieties of *Rhus* are employed in the United States for tanning and dyeing purposes, and of these the *R. glabra* (Linn.) very largely takes the place of Sicilian sumach. It contains about 25 per cent. of a tannin closely resembling gallotannin, but produces a leather of very much darker colour than the Sicilian product.

Of the other varieties, *R. typhina* (Linn.) or "Virginian sumach" (10—18 per cent.), *R. cotinoides* (Nutt.) (21 per cent.), *R. semialata* (Murr.) (5 per cent.), *R. aromatica* (Ait.) (13 per cent.) (Procter), *R. metopium* (Linn.) (about 8·2 per cent. of tannin, probably gallotannin, together with traces of both quercetin and myricetin), (Perkin, Chem. Soc. Trans., 1900, 77, 427), *R. copallina* (Linn.), *R. pumila* (Michx.), and *R. toxicodendron* (Linn.), are to be found in the States. Among these, *R. glabra* and *R. copallina* are considered to be worthy of extended cultivation.

In India, numerous species of the genus *Rhus* are known to exist (Watt's Dictionary, "Economic Products of India"), and again in Algeria the *R. pentaphylla* (Desf.) is used by the Arabs for tanning goat-skins. Finally, the *Anaphrenium argenteum* (E. Mey), (*R. thunbergii*) (Cape of Good Hope), 28 per cent. of tannin (bark), probably of the catechol class (Procter), and the *Rhodosphaera rhodanthema* (Engl.) (*Rhus rhodanthema*) (New South Wales), 9·5 per cent. of tannin (leaves), resembling gallotannin, are worthy of mention. The latter plant, also known as the "yellow cedar," closely resembles the *R. cotinus*, and it is interesting to note that although

the wood of this tree contains fisetin, $C_{15}H_4O_2(OH)_4$, the colouring matter of the leaves is quercetin, $C_{15}H_3O_2(OH)_5$, (Perkin Chem. Soc. Trans., 1898, 73, 1017).

French sumach is derived from the *Coriaria myrtifolia* (Linn.), a low deciduous shrub, native of Southern Europe, and has been referred to above as an adulterant of Silician sumach. In addition to tannin (15·6 per cent., Procter), which consists probably of ordinary gallotannin together with a little ellagitannin, it contains the poisonous glucoside *coriamyrtin* (Riban, Chem. Zeit., 1867, 663) and a trace of quercetin (Perkin, Chem. Soc. Trans., 1900, 77, 428). According to Procter, the colour of leather tanned by these leaves is very satisfactory and practically equal to that produced by genuine sumach (*R. coriaria*). It is also employed in black dyeing.

Cape sumach consists of the leaves of the *Colpoon compressum* (Berg.) (*Osyris compressa*, *Fusanus compressus*, *Thesium colpoon*), and is much used in South Africa under the name of "Pruimbast". The bush is found in the mountains, where it grows to the height of about 6 feet, and only the younger leaves are gathered. These leaves contain about 23 per cent. of tannin (Procter), which has been isolated as a hygroscopic transparent glassy mass and is probably a phlobatannin glucoside. With boiling dilute acid, a reddish-brown phlobaphene gradually separates, and on fusion with alkali protocatechuic acid is produced (Perkin, Chem. Soc. Trans., 1897, 71, 1135). In addition to tannin there is also present a considerable quantity of the quercetin glucoside *Rutin* (Osyritrin) (Chem. Soc. Trans., 1910, 98, 1776). According to Procter, this material forms a useful substitute for Sicilian sumach.

In lieu of the *Colpoon compressum*, a tanning agent known as "broach leaves" (botanical origin lacking) appears to be considerably employed in South Africa. It contains about 19·9 per cent. of tannin of the so-called "catechol" variety, together with traces of both quercetin and myricetin (Chem. Soc. Trans., 1898, 73, 384).

Russian sumach consists of the leaves of the *Arctostaphylos uva-ursi* (Spreng.) (Bearberry), and is said to contain about 14 per cent. of tannin, which, according to Perkin (Chem. Soc. Trans., 1900, 77, 424), consists of a gallotannin together with traces of an ellagitannin. Minute amounts of both quercetin and myricetin have been isolated from this material.

Considerable quantities of "sumach extract" are now manufactured for dyeing and tanning purposes from genuine Sicilian sumach, and this is usually found on the market as a brown treacly liquid of about 52° Tw. So-called *decolorised* extracts are also prepared to

compete with ordinary tannic acid, and for this purpose the addition of blood albumen to the dilute extract at about 48°, then raising the temperature to 70°, and subsequently filter-pressing, gives the most satisfactory results. Sulphurous acid again is employed to brighten the colour of extracts, and acts partly as a weak acid in decomposing the inorganic salts of the tannin or colouring matter and partly as a reducing agent. In this case it is usual to pass sulphur dioxide through the liquor before concentration (Procter).

Myrobalans.

This very important tanning material consists of the fruit or nuts of the *Terminalia chebula*, a tree of from 40—50 feet high, which grows in China and the East Indies. These nuts, which resemble a somewhat shrivelled plum, contain from 30—40 per cent. of tannin, the unripe fruit containing the largest amount. They should be bright in colour, and not soft, and require to be kept in a dry place, otherwise they absorb moisture and are then difficult to grind. The tannin present consists of a gallotannin, which is at least in part chebulinic acid, together with a fairly large amount of ellagitannin, and this, owing to fermentation and other causes, is decomposed to some extent during lixiviation into ellagic acid. Myrobalans from the dyer's point of view is one of the most serviceable tannin materials at the present time. Enormous quantities of its extract, especially as purified or decolorised extracts, are manufactured, and these are employed for cotton dyeing, in the black dyeing of silk, and in tanning.

Valonia.

Valonia (*Valonée*, Fr.; *Valonea*, *Ackerdoppen*, *Orientalische Knoppern* (Ger.)), an important tanning material, is the acorn cup of certain species of oak, usually *Quercus aegilops* (Linn.), and probably *Q. macrolepsis*, *Q. graeca*, *Q. ungeri*, and *Q. coccifera* (Linn). The former is most prolific in the highlands of Morea, Roumelia, Greek Archipelago, Asia Minor, and Palestine, whereas the *Q. macrolepsis* forms great forests in Greece. These acorn cups have a diameter up to about 1½ inches, and in good condition possess a bright colour.

The fruit ripens in Asia Minor about July or August, and the trees are then shaken, and the material left on the ground to dry; this is subsequently collected into heaps, and allowed to ferment for some weeks, until the acorn contracts and falls from the cup. The

acorn, which contains but little tannin, is employed for feeding purposes.

In Greece distinct qualities of valonia are known, the best (*chamada*) collected about April before the fruit is ripe, a second (*rhabdisto*) in September or October, and a third little-used inferior variety (*charcala*).

Smyrna valonia may contain 40 per cent., Greek 19—30, and Candia valonia 41 per cent. of tannin matter, which consists of a mixture of a gallotannin and an ellagitannin. Valonia is, indeed, an excellent source for the preparation of ellagic acid, because it so readily yields a product easy to purify. Extract of valonia frequently undergoes fermentation with deposition of ellagic acid, and to avoid this the employment of antiseptics is to be recommended.

Valonia is especially suited for the manufacture of sole leather, and together with gambier and other materials for dressing leather, but is little employed for dyeing purposes (*cf.* Procter, "Principles of Leather Manufacture," 259).

Divi-divi.

Divi-divi consists of the dried pods of the *Caesalpinia coriaria* (Willd.), a tree 20—30 feet high, found in the West Indies and Central America. The pods are about 3 inches long and ¾ inch broad, are very thin, and frequently resemble in shape the letter S. From 40—45 per cent. of tannin is present, which consists of ellagitannin and probably also a gallotannin. Extracts of this material have a somewhat unfortunate tendency to ferment, with simultaneous development of a deep-red colouring matter; but this can be prevented to some extent by the use of antiseptics. Divi-divi is largely imported for the preparation of leather, and is also employed for black dyeing, but its use is far more limited in this latter respect than myrobalans.

Algarobilla.

Algarobilla consists of the pods of the *Caesalpinia brevifolia* of Chili. The tannin appears to consist principally of ellagitannin, and this lies in resinous particles loosely attached to the somewhat open framework of the fibre. It is one of the strongest tannin matters known, and contains on the average 45 per cent. In character it resembles divi-divi, its extract being somewhat liable to fermentation. It is very suitable for tanning and also for dyeing purposes.

Quebracho colorado.

The *Quebracho colorado* are anacardinaceous trees belonging to the genus *Quebrachia*, growing in the northern part of the Argentine Republic, the wood of which constitutes the well-known tannin substance "quebracho". It is imported into this country in the form of logs and is employed for tanning, either in the chipped condition or in the form of extract. Their wood is extremely hard, as the name "quebracho" (axe-breaker) denotes, and its specific gravity varies from 1·27—1·38.

Jean (Bull. Soc. chim., 1880, 33, 6) found that it contained 15·7 per cent. of a tannic acid, not identical with that of oak bark or chestnut wood, whereas Procter ("Leather Manufacture," 1903, 269) estimates it to contain about 20 per cent. of a tannin yielding reds (phlobaphene), and containing catechol and phloroglucinol nuclei. This tannin is somewhat sparingly soluble in water and can only be used in weak liquors, but gives a firm reddish leather.

In order to isolate the tannin, Strauss and Geschwender (Zeitsch. angew. Chem., 1906, 19, 1121) extract the bark first with chloroform and then with alcohol. Addition of water to the alcoholic extract causes the separation of phlobaphenes, and from the clear liquid concentrated in a vacuum the tannin is precipitated by lead acetate, the lead salt being collected, suspended in water and decomposed with sulphuretted hydrogen. The resulting solution is evaporated to dryness, the residue dissolved in alcohol and poured into ether. Thus obtained it consists of a light flaky mass, which is hygroscopic and becomes sticky on exposure to moist air.

According to Arata (Jean, Bull. Soc. chim., 1879, 306) *quebracho tannin*, $C_{26}H_{24}O_{10}$, gives *catechol* on dry distillation, with nitric acid *oxalic* and *picric acids*, by fusion with alkali *phloroglucinol* and *protocatechuic acid*, whereas, by the latter method, Nierenstein isolated also *hydroquinone* and *resorcinol* (Collegium, 1905, 65). According to the latter author, the quebracho colorado probably contains three tannins. By treating a cold aqueous extract of the quebracho colorado with bromine, Böttinger (Ber., 17, 1123) obtained a reddish-yellow compound containing 42·1—44·5 per cent. of bromine. Nierenstein, who isolated the tannin according to Trimble's method ("The Tannins"), treated the solution with lead acetate, filtered, and on adding bromine to the clear liquid obtained a precipitate of *monobromoquebrachotannin*, $C_{16}H_{14}BrO_8$, which consists of a cinnabar red powder, and on digestion with alcoholic potash gives *isovanillic acid* and *monobromoquebrachylic acid* needles, melting-point 119—120°.

Strauss and Geschwender (*loc. cit.*) consider that quebracho tannin is identical with malettotannin, and with the tannin from cinchona bark, and ascribe to it the formula $[C_{41}H_{44}O_{18}(OMe)_2]_2$. With a mixture of acetic anhydride and acetic acid an *acetyl* compound, $(C_{30}H_{22}O_{11}Ac_6)_2$, colourless powder, is produced, and a corresponding *benzoyl* derivative, $(C_{30}H_{22}O_{11}Bz_6)_2$, can also be prepared.

Quebracho phlobaphene, on distillation with zinc-dust, yields anthracene (Nierenstein, Ber., 1907, 40, 4575).

According to Arnaudon the wood contains a colouring matter which gives a fine yellow dye, and this has been examined by Perkin and Gunnell (Chem. Soc. Trans., 1896, 69, 1304), and found to be identical with *fisetin*, the colouring matter of young fustic. This compound, which appears to exist in the wood as glucoside, gives on fusion with alkali protocatechuic acid and resorcinol, and may account for the appearance of the latter phenol among the hydrolytic products of the crude tannin itself. According to Perkin and Gunnell, when an extract of the *quebracho colorado* is digested with boiling dilute acid a small quantity of *ellagic acid* is obtained.

In addition to the tannins above described, the quebracho colorado is the source of the so-called "quebracho resin," which collects as a thickened juice in the crevices of the tree. It has been examined by Arata (Chem. Soc. Abstr., 1878, 984), who states that it is easily soluble in alcohol or ethyl acetate, insoluble in benzene. By fusion with alkali it gives *protocatechuic* acid (?) and *phloroglucin*, and by the action of nitric acid, oxalic and picric acids are produced.

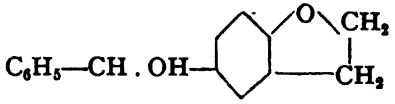
A considerable amount of the tannin contained by the *quebracho colorado* is of a sparingly soluble nature, and is deposited to some extent from a hot aqueous extract on cooling. This product may be rendered soluble by treatment with alkalis or alkaline sulphites, and a large quantity of the so-called "soluble" quebracho extracts are prepared by heating the material in closed vessels with bisulphites, sulphites, sulphides, or even caustic alkalis (Lepetit, Dollfus and Gansser, Eng. Pat., 1896, 8582; cf. Procter, "Leather Manufacture," 338).

CHAPTER XIV.

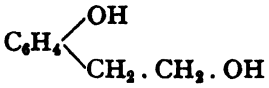
COUMARANE GROUP.

Catechu or Cutch—Cyanomaclurin—Kino.

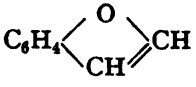
Leuco-benzoyl-coumarane—



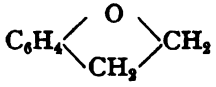
according to v. Kostanecki and his co-workers is probably the mother substance of the catechin present in Gambier catechu, though the correctness of this view has not yet been fully established. *Coumarane* or *hydro-coumarone*, the inner anhydride of *o*-hydroxyphenyl-ethyl alcohol—



was first prepared by Alexander (Ber., 1892, 25, 2409) by reducing coumarone in alcoholic solution with sodium—

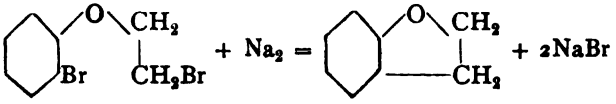


Coumarone.

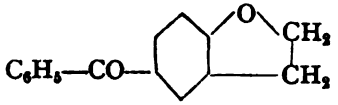


Coumarane.

It forms a colourless oil, boiling-point 188—189°, and gives in sulphuric acid solution by addition of ferric chloride a violet coloration. Stoermer and Göhl (Ber., 1903, 36, 2873) have obtained coumarane and its homologues by the action of sodium on *o*-bromo-phenol brom-ethyl esters according to the following equation :—



By the interaction of coumarane and benzoyl chloride in the presence of aluminium chloride, 4 benzoyl-coumarane colourless crystals, melting-point 44°—



is produced (v. Kostanecki, Lampe and Marschalk, Ber., 1907, 46, 3660), and when reduced in alcoholic solution, the leuco-benzoyl-coumarane above referred to is obtained.

Catechu or Cutch.

There are several varieties of catechu or cutch bearing different names according to the country or plants from which they are obtained. The following are those principally employed by dyers and tanners: Gambier catechu, Bengal or Acacia catechu, Bombay or Areca catechu, and Mangrove cutch.

Although catechu has perhaps received greater attention than other natural dyes, the results have been so varied that the chemistry of the subject was until recently in a most unsatisfactory condition. Some confusion has arisen from the non-appreciation of the fact that the main constituents of gambier and Acacia catechu are not identical, and some uncertainty has also apparently existed as to the botanical origin of the commercial varieties. Bombay catechu is, for instance, occasionally referred to as originating from the *Acacia catechu*, and *Bengal catechu* from the *Areca catechu* (Linn.); and in many cases, at the present time, it is impossible to ascertain the botanical derivation of commercial brown cutch preparations.

Gambier catechu.—Gambier, yellow cutch, cubical cutch, cube gambier, or terra japonica, is obtained from the *Uncaria gambier*, an extensive scandent bush which is met with, both wild and cultivated, in Malacca, Penang, and Singapore. The catechu is isolated by extracting the leaves and twigs with hot water until the liquid becomes syrupy, the insoluble matter being removed from time to time by means of a strainer. On cooling, the pasty mass is cut into cubes with sides 1 inch in length and dried on bamboo trays.

Catechin, $C_{15}H_{14}O_6$, $4H_2O$, the crystalline principle, was first described by Nees van Esenbeck (Annalen, 1832, 1, 243), was subsequently examined by Berzelius in 1837 (Jahres., 14, 235), and more recently by numerous chemists. To isolate catechin, Löwe (Zeitsch. anal. Chem., 13, 113) devised the following method: catechu is washed with cold water to remove catechutannic acid, well pressed,

allowed to dry, and dissolved in hot acetic ester. The filtered solution is evaporated and the residue crystallised from hot water.

According to Perkin and Yoshitake (Chem. Soc. Trans., 1902, 81, 1162), a combination of this method and that of Berzelius (*loc. cit.*) gives good results.

The finely powdered catechu is extracted with 10 times its weight of boiling ethyl acetate, the solution is evaporated, and the residue crystallised from 10 times its weight of water. The product is again dissolved in boiling water, and lead acetate solution added, drop by drop, until a coloured precipitate is no longer formed, and the filtrate is almost colourless; the latter, while hot, is treated with sulphuretted hydrogen, the lead sulphide removed, and the crystals, which separate on cooling, are collected, washed, and allowed to dry at the ordinary temperature. The substance is now practically colourless, and the yield greater than if the purification had been effected by frequent crystallisation from water.

The formulæ which have been assigned to catechin are very numerous, and it has only recently been shown by v. Kostanecki and Tambor (Ber., 1902, 35, 1867), and simultaneously by Perkin and Yoshitake (*loc. cit.*), that it is correctly represented as

$$C_{15}H_{14}O_6, 4H_2O$$

Catechin forms colourless needles, and when crystallised from water the air-dry product melts at 96° (Clauser, Ber., 1903, 36, 101). After standing over sulphuric acid, it possesses the formula

$$C_{15}H_{14}O_6, H_2O,$$

and melts at 176—177°, and this is also the melting-point of the anhydrous substance. Catechin is readily soluble in boiling water and cold alcohol, and gives with lead acetate solution a colourless precipitate, and with ferric chloride a deep green liquid. With pine wood and hydrochloric acid, it gives the phloroglucinol reaction.

On fusion with alkali, *protocatechuic acid*, *phloroglucinol*, and probably acetic acid are produced, and it is interesting to note that catechu has been considerably employed for the commercial preparation of the former compound.

Schützenberger and Rack (Bull. Soc. chim., 4, 6) have described a dibenzoylcatechin; and Liebermann and Tauchert (Ber., 1880, 13, 695), diacetyl catechin, diacetyl dichlorcatechin, and diacetyl dibromcatechin; but their formulæ for these compounds are now known to be incorrect.

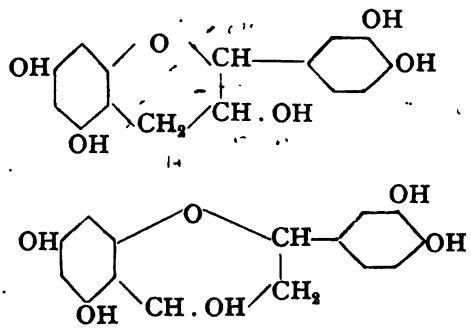
Penta-acetyl-catechin, $C_{15}H_9O_6(C_2H_3O)_5$, colourless needles,

melting-point 124—125° (v. Kostanecki and Tambor); *pentabenzoyl catechin*, $C_{15}H_9O_6(C_7H_5O)_5$, colourless needles, melting-point 151—153°; *tetrabenzoyl-catechin*, $C_{15}H_{10}O_6(C_7H_5O)_4$, prisms, melting-point 171—172° (Perkin and Yoshitake); *disazobenzene-catechin*, $C_{15}H_{12}O_6(C_6H_5N_2)_2$, salmon-red needles, melting-point 193—195° (Etti, Perkin and Yoshitake); *acetyldisazobenzene-catechin*, orange-red needles, melting-point 253—255° (Perkin and Yoshitake); *catechin tetramethylether*, $C_{15}H_{10}O_2(OCH_3)_4$, needles, melting-point 144—146° (v. Kostanecki and Tambor); *acetyl-catechin tetramethylether*,

$$C_{15}H_9O_2(OCH_3)_4C_2H_2O,$$

needles, melting-point 92—93°; and *catechin pentamethylether*, $C_{15}H_9O(OCH_3)_5$ (v. Kostanecki and Tambor), have been prepared.

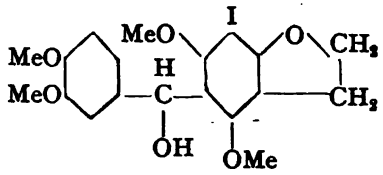
When catechin tetramethylether, suspended in water, is oxidised with potassium permanganate, it gives *veratric acid*, and most probably *phloroglucinol dimethylether* (Chem. Soc. Trans., 1905, 87). As the result of this investigation, Perkin considered that catechin was possibly a reduction product of quercetin—



or

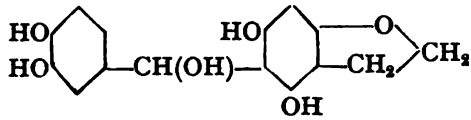
and indeed a small quantity of the latter colouring matter is present in catechu (Löwe, Perkin, *ibid.*, 71, 1135).

More recently v. Kostanecki and Lampe (Ber., 1906, 39, 4007) have shown that when catechin tetramethylether is brominated in the presence of sunlight, only a *monobromcatechin tetramethylether*, melting-point 173—174°, is produced, whereas the above constitutional formulæ require the formation of a dibromo compound. When oxidised with permanganate, bromcatechin tetramethylether gives veratric acid, so that the bromine must have replaced one hydrogen of the phloroglucinol nucleus. When alcoholic solutions of catechin-tetramethylether and of iodine and iodic acid are mixed, long colourless needles of *iodocatechin-tetramethylether* separate after a few hours—

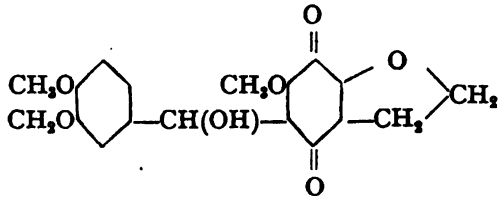


melting-point 192—193° C.; this yields an *acetyl derivative*, $C_{21}H_{22}O_7I$, melting-point 189° C.

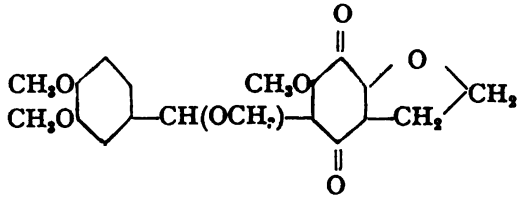
Iodocatechin-tetramethylether when treated with zinc-dust and alkali yields the original catechin-tetramethylether, this elimination of iodine being also noticed with other members of the maclurin type (v. Kostanecki and Lampe, Ber., 1907, 40, 4910). v. Kostanecki and Lampe have assigned the following constitution to catechin :—



and this is in harmony with many of the properties of this substance. When catechin tetramethylether is oxidised with chromic acid, *catechone trimethylether*, orange-yellow needles, melting-point 210°, is produced (v. Kostanecki and Tambor)—

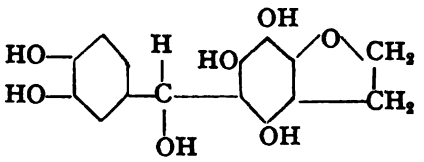


whereas catechin pentamethylether gives the tetramethyl compound—



and this behaviour is analogous to that of leucomaclurin pentamethylether (see Maclurin).

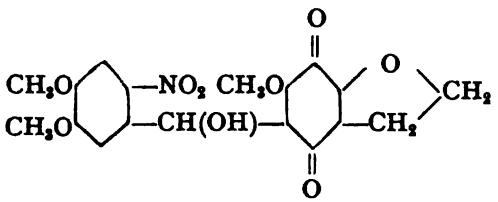
Acetyl catechone by reduction with zinc-dust and glacial acetic acid, and hydrolysis of the product, gives *hydroxy-catechin*, yellow needles, melting at 284—285° C.—



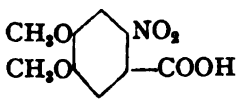
The hexamethylether has melting-point 102° C. (Nierenstein, Annalen, 1903, 396, 194).

When catechone trimethylether is nitrated, a mononitro derivative (1)—

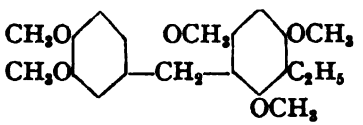
(1)



(2)



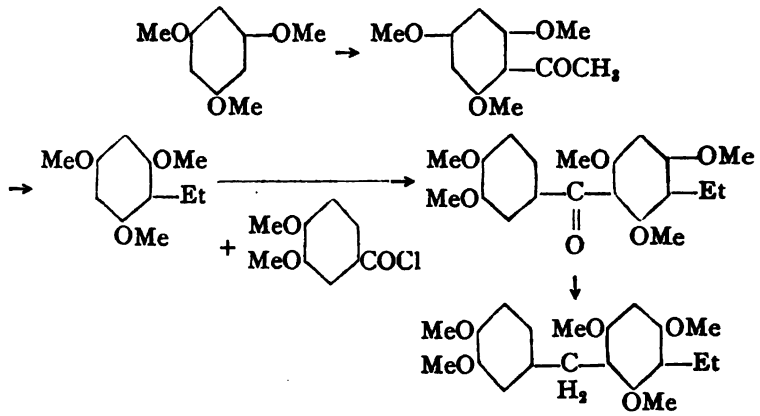
melting-point 141°, is obtained, and on oxidation yields nitroveratric acid (2). Finally, by the reduction of catechin tetramethylether with sodium and alcohol, an oil is produced which, on treatment with methyl sulphate, gives *pentamethoxyethyldiphenylmethane*—



a reaction which points apparently to the presence of the cumaran ring in catechin.

Ryan and Walsh (Proc. Roy. Dub. Soc., 1916, 15, 113) have attempted to decide between the chroman structure of Perkin and Yoshitake and the coumaran formula of v. Kostanecki and Lampe. To this end they have synthesised 2 : 4 : 6 : 3′ : 4′-penta-methoxy-3-ethyl-diphenyl-methane, in order to ascertain whether this was identical with the deoxy-hydro-catechin-penta-methyl-ether obtained from catechin, as described above by v. Kostanecki and Lampe.

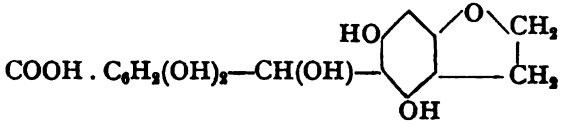
The synthesis is made clear by the following scheme :—



They were, however, unable to obtain the resulting product in a crystalline condition—the addition of a crystal of the product obtained from catechin (deoxy-hydrocatechin-pentamethyl-ether) failed to cause it to crystallise—hence they were not able to obtain a definite settlement of this point.

Catechin is oxidised in aqueous solution by potassium ferricyanide in the presence of potassium acetate with formation of an orange-coloured amorphous compound (Perkin) which dyes mordanted calico orange-brown shades which are fairly fast to soap. It is probable that this dyestuff is related to the catechone of v. Kostanecki and Tambor, and which was obtained by these authors in the form of its tri- and tetramethyl ethers.

When catechin is treated with carbon tetrachloride and aqueous potassium hydroxide, it yields *catechin carboxylic acid*, colourless needles, melting-point 274—277° C. (decomp.)—



The annexed constitution has been assigned to it on account of the fact that its *penta-methyl-ether methyl-ester*, $C_{22}H_{26}O_8$, melting-point 92° C., when oxidised with alkaline permanganate yields hemipinic acid.

Catechin carboxylic acid has been resolved, and the *d*-acid has $[\alpha]_D^{18} = + 76{\cdot}4°$, and melting-point 273° C. (decomp.), whilst the *l*-acid gave values $[\ ]_D^{18} = - 68{\cdot}22°$, and melting-point 270—273° C. (decomp.), (Nierenstein, Annalen, 1913, 396, 194).

Catechutannic acid.—In addition to catechin, gambier catechu contains a small amount of catechutannic acid, and this substance is present in considerable quantity in the browner varieties of cutch. To isolate it the following method has been employed :—

A hot aqueous extract of catechu is allowed to stand until no more catechin is deposited, and the clear liquid is evaporated to dryness. The residue is dissolved in alcohol, the solution treated with ether to precipitate impurities and then evaporated to dryness.

Catechutannic acid consists of an amorphous reddish-brown powder, readily soluble in water and alcohol, insoluble in ether. According to Löwe (Fr., 13, 121), it possesses the formula $C_{21}H_{18}O_8$, and gives a lead salt $3PbO, 2C_{21}H_{18}O_8$, but this most probably requires revision.

According to Etti (Annalen, 186, 332) catechutannic acid is an anhydride of catechin, and is derived from this substance by elimination of water. It is said to be produced when an aqueous solution of catechin is heated to 110° (Löwe, *ibid.*, 12, 285), or by boiling catechin with solutions of the alkali carbonates. Again, catechin is decomposed at its melting-point with evolution of water and formation of a product resembling catechutannic acid, and aqueous solutions of catechin on long standing become brown-coloured with apparent formation of this compound. That the products obtained by these methods resemble catechutannic acid is certain, but the subject has not been fully investigated.

Catechutannic acid solution gives a precipitate with lead acetate, and also resembles catechin in giving a green coloration with ferric chloride; and the phloroglucinol reaction with pinewood and hydrochloric acid. It is a powerful tanning agent, and appears to differ but little from the so-called "catechol" tannins.

Three other catechin anhydrides have been described, viz. the *second* anhydride, $C_{42}H_{34}O_{15}$ (?), (Etti), which is produced by heating catechutannin to 162°; the *third* anhydride, $C_{21}H_{16}O_7$ (?), formed by digesting catechin with boiling dilute sulphuric acid for several hours; and the *fourth* anhydride, which is obtained by heating catechin with hydrochloric acid at 160—180°. These compounds consist of reddish-brown powders, and the fourth substance is insoluble, both in alkaline solutions and all solvents. A product similar in properties to Etti's fourth anhydride is readily formed by adding sulphuric acid to a hot acetic acid solution of catechin (Perkin). A bright orange powder almost immediately separates, and this, on analysis, gave C = 63·26 per cent.; H = 3·89 per cent. It is

interesting to note that the formation of these red anhydrides, or *phlobaphenes*, is characteristic of all the catechol (phlobo) tannins.

According to Perkin and Yoshitake, gambier catechu contains a small quantity of a second catechin, which crystallises in small prisms, devoid of water of crystallisation, and melts at 235—237°. Its general reactions are identical with those of ordinary catechin, and by fusion with alkali it also gives *phloroglucinol* and *protocatechuic* acid. The azobenzene compound, $C_{15}H_{12}O_6(C_6H_5N_2)_2$, orange-red needles, melts at 215—217°.

Finally, there are present in catechu certain brown substances known as *rubinic* and *japonic* acids, which, according to some writers, appear to have been formed by the oxidation of the catechin. Their chemical nature is, however, unknown.

Catechin, though largely employed for tanning purposes, does not precipitate a gelatine solution, and is not itself a tannin matter. On the other hand, it is absorbed by the hide, and there gradually passes into catechutannic acid.

Dyeing Properties.—On cotton, catechu is largely used for the production of the well-known "catechu brown," which is exceedingly fast to light, acid and alkaline solutions, and also to bleaching powder. To obtain this, cotton is steeped in a hot solution of catechu (1—2 per cent.) to which has been added about 6 per cent. of copper sulphate, reckoned on the weight of the catechu employed. The material is allowed to remain in the bath as it cools, and without washing is then treated in a warm or boiling second bath containing 1 or 2 grams of bichromate of potash per litre. According to Hummel and Brown (J. Soc. Chem. Ind., 1896, 15, 422), in this operation the copper sulphate probably converts the catechin into catechutannic acid, and this is subsequently oxidised to japonic acid by the action of the bichromate. The colour is apparently intensified by the formation of a basic copper chromate. Gambier catechu is also employed in dyeing compound shades with logwood, fustic, and alizarine in conjunction with bichrome, and with bismarck brown, magenta, etc. In the latter case catechu-tannin forms the mordant for the basic colour.

Wool may be dyed with catechu in a similar manner to cotton. In silk dyeing, catechu is largely used for weighting purposes. The silk is steeped in basic ferrous sulphate solution, then in potassium ferrocyanide and hydrochloric acid, which causes the production of prussian blue on the fibre. It is then worked in a strong solution of gambier to which stannous chloride solution has been added.

Bengal or Acacia Catechu.—Bengal catechu is derived from the

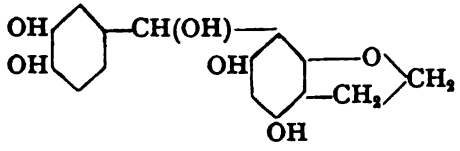
Acacia catechu, a tree 15 to 20 feet high, which is common in most parts of India and Burma. To isolate the catechu which is present in the red heartwood, the tree is cut down while it is fullest of sap, and the internal portion is sawn into small sticks and extracted with boiling water. The liquid thus obtained is concentrated over a fire, and then allowed to evaporate spontaneously in shallow dishes. The extract thus obtained comes into the market as *Pegu* catechu, brown cutch, and brown catechu (Crookes, "Dyeing and Calico Printing").

A purer substance, *kath*, or the pale catechu of India, is prepared by suspending twigs in the hot concentrated extract and collecting the crystals which thus separate.

Acacatechin, $C_{15}H_{14}O_6$, $3H_2O$, can be obtained from the acacia kath by methods identical with those which are employed for the isolation of catechin from gambier catechu. It melts at 204—205°, is somewhat more sparingly soluble in water than catechin, and when fused with alkali gives *phloroglucinol* and *protocatechuic acid*. The reactions of acacatechin and catechin, in so far as they have been observed, are identical, and there is no difference in the composition of their derivatives when prepared under similar conditions. On the other hand, the melting-points of the substances themselves, and also of their derivatives, differ widely, as is evident from the following table (Perkin and Yoshitake) :—

	Acacatechin.	*Catechin.*
Penta-acetyl derivative. .	158—160°	124—125°
Pentabenzoyl „ . .	181—183°	151—153°
Azobenzene „ . .	198—200°	193—195°
Tetramethyl „ . .	152—154°	144—146°
Acetyl „ . .	135—137°	92—93°

It appears certain, therefore, that catechin and acacatechin are isomerides, and it is possible that the latter may, on the basis of v. Kostanecki and Lampe's formula for catechin, be represented thus (Perkin, private communication) :—



a point which should not be difficult to determine.

Bombay or Areca Catechu.—This variety is obtained from the fruit of the *Areca catechu* or betel-nut palm, a tree which is common

in tropical Asia. Though its chief constituent resembles catechu-tannic acid, catechin itself has not been isolated from this product. It possesses a bright chocolate and sometimes an orange-brown colour, and yields, on dyeing, very similar results to the ordinary cutches.

Mangrove cutch is obtained from the bark of the mangrove *Ceriops candolleana*, and is of somewhat recent employment. In its preparation it is preferable to extract the fresh bark, which is of a light colour internally, rather than the stored product which has become red, or is said to have "sweated". The extract, on evaporation, becomes deep-red in colour, and the object of the manufacturer is to prevent this anhydride formation from going too far, otherwise a certain portion of the extract is rendered insoluble in water.

By fusion with alkali, it gives *protocatechuic acid*, but at present no catechin has been isolated from it (Perkin, private communication). When dissolved in sodium bicarbonate solution, acetic ester extracts an almost colourless tannin, which possesses the properties of a catechol tannin.

For many purposes, mangrove cutch is competing closely with the other varieties of catechu, and this competition will no doubt become keener, if its quality can be further improved.

Mahogany.—According to Caseneuve (Ber., 8, 828) mahogany wood contains a catechin. (See also under Rhubarb tannic acid, p. 449.)

CYANOMACLURIN.

Cyanomaclurin, $C_{15}H_{12}O_6$, a colourless compound existing in Jak-wood, is closely allied to the catechins, and may possibly belong to the same group. In its general reactions, indeed, it is very similar to these compounds, but differs from them in that by alkali fusion it yields *β-resorcylic acid* and not protocatechuic acid.

A full description of the properties of this compound is given in the article on Jak-wood.

KINO.

Kino consists of the dried astringent juice of various trees, and though now practically obsolete, came into commerce in the form of small semi-opaque reddish-brown fragments. There are numerous varieties of this material, of which the following are the best known :—

Malabar kino (*Pterocarpus marsupium*), African or Senegal kino (*Pterocarpus erinaceus*), West Indian kino (*Coccoloba uvifera*),

Bengal kino (*Butea frondosa*), and Australian kino (*Eucalyptus spec*). Among these, Malabar kino, at one time medicinally employed in Europe owing no doubt to its astringent properties, appears to have been the most frequently examined, though as the results obtained by distinct workers have not always been in agreement, it is probable that material experimented with has in certain cases consisted of some other variety.

When distilled Malabar kino evolves catechol (Eissfeld, Annalen, 1854, 92, 101), and by fusion with potassium hydroxide, *phloroglucinol* and *protocatechuic acid* are obtained.

According to Etti (Ber., 1878, 11, 1879) when kino is digested with dilute hydrochloric acid, and the liquid extracted with ether, a substance *kinoin*, $C_{14}H_{12}O_6$, crystallising in colourless prisms, can be isolated. This compound is readily soluble in hot water, and when heated with hydrochloric acid to 130° yields catechol, gallic acid, and methyl chloride, and at 120° is converted into an amorphous red compound, $C_{28}H_{22}O_{11}$, the so-called kino red. Kino red is itself present in kino and forms a red resinous powder sparingly soluble in water, and the solution thus obtained gives a dull green coloration with ferric chloride.

Perkin (Chem. Soc. Trans., 1902, 81, 1173) obtained in a similar way from a sample of kino (botanical origin uncertain) a small amount of crystalline substance, which he regarded as kinoin, and which possessed yellow dyeing properties with aluminium mordanted calico.

White, however (Pharm. J., 1903, (ix.), 16, 676), was unable to obtain kinoin from Malabar kino, and again, Simonsen (Chem. Soc. Trans., 1911, 99, 1532), who submitted material of undoubted botanical authenticity to critical examination, could only isolate a small amount of catechol by Etti's method. From kino itself Simonsen, by the action of methyl sulphate and potassium hydroxide, obtained the *trimethyl ether*, $C_{15}H_{11}O_4(OMe)_3$, a colourless amorphous powder which could not be crystallised. That kino thus contains three hydroxyl groups was confirmed by an examination of the *acetyl* derivative, an amorphous brown powder of the formula

$$C_{15}H_{11}O_4(OAc)_3$$

By oxidation with permanganate, kino methyl ether yields *veratric* acid, whereas by fusion with alkali, kino itself gives *protocatechuic acid*. By neither of these decompositions could the formation of phloroglucinol or a phloroglucinol derivative be detected, and the statement of Eissfeld that he obtained phloroglucinol from

kino appears, therefore, to be incorrect. Smith (Roy. Soc. N.S. Wales, 1895, 30, and 1896, 135) isolated from Australian kinos derived from *Eucalyptus hemiploia* (F. and M.) and *E. calophylla* (R. Br.), by means of ether, a substance *aromadendrin*, melting-point 216°, to which the formula $C_{29}H_{26}O_{12}$ was assigned. This crystallises from water in colourless needles resembling catechin in appearance, soluble in alkalis with a yellow colour, and gave with lead acetate a yellow coloured precipitate, and with ferric chloride a purple-brown coloration. When heated in glycerol solution, or above its melting-point, aromadendrin gives kino yellow, a yellow resinous substance almost insoluble in cold water. It is, however, easily soluble in alcohol, and this solution possesses great staining power and dyes wool and skin a bright yellow colour.

Butea Gum.

The dried juice of *Butea frondosa* (Roxb.) is often sent into the market instead of genuine kino. It forms black-brown, slightly lustrous, brittle lumps, has an astringent taste, and yields catechol by dry distillation.

CHAPTER XV.

INDOLE GROUP.

Natural Indigo—Properties and Syntheses of Indigotin—*Lonchocarpus cyanescens*—Woad—Purple of the Ancients.

NATURAL INDIGO.

INDIGO has been known in Asia from a remote period of antiquity, and there exist very ancient records in Sanskrit describing its methods of preparation. The Romans appear to have recognised it only as a pigment (*indicum*), but evidence as to its use as a dye by the ancient Egyptians has been abundantly proved from the examination of mummy cloths. Its employment in Europe was very limited until in 1516 when it began to be imported from India by way of the Cape of Good Hope, but its introduction in large quantity did not occur until about 1602. Owing chiefly to the opposition of the growers of woad, its European rival, as a dyeware it met with much opposition, and various laws were enacted both on the Continent and in England prohibiting its use. It was called a "devilish drug," and was said to be injurious to fabrics. In 1737 its employment was legally permitted in France, and from this period its valuable properties appear to have become gradually recognised throughout Europe.

The most important plants which yield indigo are those of the genus *Indigofera* belonging to the natural order of the *Leguminosæ*; these have been cultivated in India, China, Egypt, the Philippines, Caracas, and Brazil.

For the purpose of indigo manufacture the *Indigofera tinctoria* (Linn.), *I. sumatrana* (Garrtn.) (the Indian plant), *I. disperma* (Linn.), *I. argentea* (Linn.), and *I. arrecta* (Hochst.) (the Natal plant), the *I. paucifolia* (Delile) (Madagascar plant), and *I. secundiflora* (Poir.) (Guatemala plant), have been mainly used, though certain less valuable varieties, viz. the *I. pseudotinctoria* (R. Br.), *I. angustifolia* (Linn.), *I. arcuata* (Willd.), *I. caroliniana* (Walt.), *I. cinerea* (Willd.), *I. longeracemosa* (Boiv.), *I. cærulea* (Roxb.), *I. endecaphylla* (Jacq.),

I. glabra (Linn.), *I. hirsuta* (Linn.), *I. indica* (Lam.), *I. mexicana* (Benth.), *I. leptostachya* (DC.), have been employed. In Japan, China, and Russia the plant usually cultivated has been the *Polygonum tinctorium* (Ait.), but the *Isatis tinctoria* (Linn.), or woad plant, at one time very largely grown in Europe, is now only used in very limited quantity as an adjunct in the dyeing of indigo (woad vat). The native source of indigo in Western Africa appears to consist almost entirely of the *Lonchocarpus cyanescens* (Benth.) (Perkin, J. Soc. Chem. Ind., 1904, 26).

Other indigo-yielding plants are the *Nerium tinctorium*, *Gymnema tingens* (Spreng.), *Eupatorium laeve* (DC.), *Tephrosia tinctoria* (Pers.), *Marsdenia tinctoria* (R. Br.), and certain species of orchids such as the *Phaius grandiflorus* (Reich.), and *Calanthe veratrifolia* (R. Br.).

In addition to these, various plants, of which the *Mercurialis perennis* (Linn.), *Fagopyrum esculentum* (Moench.), *Fraxinus excelsior* (Linn.), *Baptisia tinctoria* (R. Br.), and *Rhamnus alaternus* (Linn.) (Georgievics, Der Indigo, 1892) may be given as examples, are stated to yield indigo, or a very similar colouring matter, but this requires confirmation.

The production of indigo from the indigo plant is of a simple character and consists mainly of two processes, viz. a steeping of the plant with water (fermentation), followed by the oxidation of the solution with air in a separate vessel. Until very recently but little modification appears to have been introduced into this ancient process, and there is also but little variation to be found in the main features as described by Bancroft ("Philosophy of Permanent Colours," 1813), Crookes ("Manual of Dyeing and Calico Printing," 1874), Bridges-Lee ("Indigo Manufacture," 1892), Georgievics (*loc. cit.*, 1892), and Rawson ("The Cultivation and Manufacture of Indigo," J. Soc. Dyers, 1899).

Directly the plants are cut down they are tied in bundles and brought to the factory without delay, because it is necessary that the material should be operated on at once.* The tanks for the extrac-

* It has long been known that the percentage of indican rapidly disappears from the leaf in the freshly plucked moist condition, and on this account it is advisable that the plant when cut down should be dealt with at once. On the other hand, it has been the practice to a small extent in certain districts to air-dry the leaf before proceeding with the manufacture of indigo. In order to determine if when air-dried under ideal conditions, the leaf in these circumstances loses a material amount of indican, experiments were made by Watson (Jour. Chem. Soc. Ind., 1918, 37, 81) with indigo plant specially grown for the purpose. The leaf when gathered was divided into two portions, one of which was analysed

tion (steeping vats) and precipitation of the indigo by oxidation (beating vats) are sometimes of stone, but more usually of brick-work lined inside with cement, and are respectively ranged in two rows one above the other, so that the former can be drained into the latter. The steeping vats may have a capacity of about 1000 cubic feet, and are usually of much smaller dimensions than the beating vats, of which less are consequently required. According to Rawson (*loc. cit.*), who describes a small indigo factory, each range of beating vat runs the whole length of six steeping vats, and has a width of 13 feet 6 inches.

Into each of the upper tanks the bundles of the plant are tightly packed (preferably in a horizontal position, Bridges-Lee, *loc. cit.*), on the top of this is laid a horizontal trellis of bamboo, and the whole is wedged down into the tanks by means of timber, so that the material is unable to float during the fermentation process. Water is then run in, in such quantity that the bundles are entirely submerged. After about two hours an active fermentation is observed, and the surface of the liquid becomes covered with froth owing to the evolution of a mixture of carbon dioxide, oxygen, and nitrogen (Georgievics, *loc. cit.*); in the later stages (Rawson, *loc. cit.*) either marsh gas or hydrogen or a mixture of the two is freely produced. After ten to fifteen hours, according to the prevailing temperature of the water, the straw-yellow, orange, or olive-green coloured liquid is drawn off into the tanks below, and submitted to oxidation with air.

This may be accomplished by "hand beating," by machinery (the beating wheel), by blowing air through the liquid, or by the shower-bath method. During this operation the colour of the liquid gradually changes, becoming first dark green and then blue, and considerable frothing is produced. When it is observed that the indigo precipitate or "fecula" readily settles, the beating is discontinued and the mixture allowed to rest for some two hours. The supernatant liquid, or "seeth water," having been drained off as completely as possible, the indigo sludge or "mal" is led into a reservoir

at once, and the second dried by spreading in a thin layer upon filter paper in a north verandah for three or four days until constant in weight.

The analyses were carried out by the isatin method (*loc. cit.*) with 10 grammes of leaf weighed in each case in the fresh condition, and the results expressed as indirubin indicate that a serious loss of colouring principle does occur in these circumstances:—

	Fresh Leaf.	*Air-dried Leaf.*
(*a*)	0·1008	0·0568
(*b*)	0·0825	0·0610
(*c*)	0·1057	0·0763

inside the factory, from which it is subsequently elevated by means of a hand pump or steam injector into a large cauldron known as the "mal boiler". It is here heated by direct fire or by the admission of steam, and this has for its object the prevention of a further fermentation, the solution of certain brown impurities, and a more complete granulation of the "mal".

The product is then run on to a filter known as a "table," consisting of stout cotton or linen cloth stretched over a shallow rectangular basin of stone or cement, with a drainage opening at one corner, and allowed to remain until it has the consistency of a stiff paste. In order to remove excess of moisture the indigo is transferred to perforated wooden boxes lined with sail cloth and cautiously pressed. Finally, the resulting slab is cut into cakes by means of a guillotine or metal wires and allowed to dry at the ordinary temperature on trellis-work shelves in a specially constructed drying house.

The Plant.

Until the last few years the *I. sumatrana* appears to have been exclusively employed in the best-conducted factories in India. According to Leake (Report of the Dalsingh Serai Research Station, 1903-1904) this is a mixture of several sub-varieties of different values. In this, as in apparently all other indigo plants, the indican exists exclusively in the leaf, though Bloxam and Leake (*loc. cit.*) point out that the midrib or rachis also contains the glucoside. For the manufacture of indigo the main points in connection with the plant are the weight yielded per acre, the percentage of leaf present, and the indigotin producing value of the latter. According to Rawson ("Cultivation and Manufacture of Indigo," *loc. cit.*) the good plant contains 40 per cent. of leaf, though occasionally, but not often, the proportion of leaf rises to as much as 60 per cent. Bloxam and Leake found, however, much higher values, 51·7—61·6 on ordinary Indian plant, and 65 per cent. given by twelve experimental plots, figures which include the rachis. Bergtheil (Report of the Indigo Research Station, Sirsiah, 1906, 8) found the percentage of leaf to be 40 per cent., and never higher than 45 per cent.; but, on the other hand, in a redetermination, Leake (J. Soc. Chem. Ind., 1907, 26, 1174) records the value as 62·2 per cent. Rawson, who conducted numerous analyses of the leaf by his persulphate process (*loc. cit.*), shows that the indican content as expressed by indigo yielding capacity varies at different periods of the year. Thus, whereas in one instance on May 28 the

figure was 0·20 per cent., on August 25 this had risen to 0·76 per cent. of indigotin. Though the leaf on a young plant gives but a small percentage of colouring matter, yet as the plant grows the new leaf contains more colouring principle than the old on the same plant. As an example, on one occasion the percentages of indigotin recorded with new and old leaf were respectively 0·71 and 0·35 per cent. Finally, there is a gradual increase in colouring matter given by leaves from the bottom of the plant upwards as represented by the figures 0·30, 0·44, and 0·62 per cent. respectively. According to Bergtheil (Report of the Indigo Research Station, 1907, 3) the "indigotin content" of the plant is rarely so high as 0·3 per cent. Though the leaf, as a rule, contains a maximum of colouring matter from about the middle to the end of August, it does not necessarily follow that this is the best period for manufacture, as by this time the plant will usually have lost a considerable portion of leaf (Rawson). The manufacture, indeed, usually commences about the middle of June. Gaunt, Thomas, and Bloxam (J. Soc. Chem. Ind., 1907, 26, 1174) refer to a sample of the air-dried leaves of the *I. sumatrana*, which, in comparison with other dry samples of the same variety (0·6 approx.) and of the Java plant, *I. arrecta* (1·81 per cent.), yielded indigotin to the value of 3·53 per cent., and consider that this indicates that by selection and suitable methods of cultivation it should be possible to obtain an average plant of greater indigo-producing power than has hitherto been the case.

The plant formerly employed by the Java planters was the *I. secundiflora*, "Guatemala plant," but for several years past this has been replaced by the *I. arrecta* or "Natal plant". The latter, it is stated, contains not only more leaf than the ordinary Indian plant, but, as a rule, the leaf yields also a considerably larger percentage of indigo. More recently the Indian planters have recognised the value of the *I. arrecta*, and accounts are given by Coventry (Indigo Improvements Syndicate Report, 1901) of experiments in connection with its introduction. Leake (Dalsingh Serai Report, 1905) discusses the difficulties of the germination of the seed of the Natal-Java plant, which is due to the impermeable character of the seed coat. This defect, it is pointed out, can be overcome by a process of scratching, and a practical method for this purpose is described. Bergtheil (*loc. cit.*), in conjunction with D. L. Day, treats the seed with strong sulphuric acid, which leads either to a swelling of the seed coat and its eventual rupture or converts it into a body akin to cellulose and permeable to water. Analyses of the indigo-yielding power of this leaf by Rawson (*loc. cit.*) gave figures up to 0·96 per

cent., whereas Bergtheil (*loc. cit.*, 1906) finds in comparison to the *I. sumatrana* (0·585) that the *I. arrecta* produced 1·05 per cent. of colouring matter. The percentage of leaf given by the latter averages 52·2 per cent. Again, in 1909 the yield from 100 maunds of the *I. arrecta* was 15 seers 10 chittacks, as against 11 seers 14 chittacks from the same quantity of the *I. sumatrana*. The Natal plant is now established in India, and its value appears to be fully recognised. According to Bergtheil (1907) the indigo made from the Java plant has generally been of a high indigotin content, and (1906) that whereas the yield of indigo per acre was 12·6 "seers," that given by the *I. sumatrana* was by comparison only 8 seers.

A full account of much detailed work on the cultivation of the indigo plants by Rawson, Bloxam and Leake, and Bergtheil is given in the reports above enumerated (*cf.* also Bergtheil, *ibid.*, 1908—1911).

The Chemistry of Natural Indigo Manufacture.

According to the early researches of Chevreul (Ann. Chim. Phys., 1808, 66, 8, and 1808, 68, 284) and of Geradin and Preisser (J. Pharm. Chim., 1840, 26, 344) the colouring principle of indigotin present in indigo-yielding plants was considered to consist of indigo white, and this theory remained uncontradicted until Schunck (Phil. Mag., 1855, [iv.], 17, 74, and 1858, 15, 127) isolated from the *Isatis tinctoria* (woad), *Polygonum tinctorium*, and *Indigofera tinctoria* (Schunck and Roemer, Ber., 1879, 12, 2311) a glucoside, which was named indican.

To prepare this substance from woad the leaves were extracted with cold alcohol, the solution treated with a little water, and concentrated at the ordinary temperature by blowing air over it. The waxy matter which thus separated was removed by filtration, and the filtrate shaken up with freshly precipitated cupric hydroxide. The mixture was filtered, the liquid freed from dissolved copper by means of sulphuretted hydrogen, and then evaporated at the ordinary temperature. The residue was extracted with cold alcohol, the extract treated with ether to precipitate certain impurities, and the solution evaporated.

Thus obtained it consisted of a yellow or yellowish-brown syrup, which was of an exceedingly unstable nature, and could not be dried without decomposition. With alcoholic lead acetate it gave a yellow precipitate, whereas in aqueous solution it could only be precipitated by means of basic lead acetate. Analyses of the lead compound

indicated that indican possessed the formula $C_{26}H_{31}NO_{17}$. Schunck found that this compound was a glucoside, and that by the action of dilute acids, alkalis and of a ferment present in the plant, it was readily hydrolysed with the formation of indigotin, and a sugar *indiglucin*—

$$2C_{26}H_{31}O_{17}N + 4H_2O = C_{16}H_{10}O_2N_2 + 6C_6H_{10}O_6$$

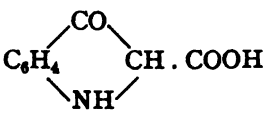
For the production of indigotin the presence of air or other suitable oxidising agent was however necessary, and it appeared, therefore, that during the reaction the indigotin at first formed was reduced to indigo white.

Later, however, Schunck and Roemer showed (*loc. cit.*) that indican, when hydrolysed in the absence of air, gave a product which, on subsequent treatment with oxidising agents, did not yield indigotin. Schunck further obtained by the action of cold dilute acids on his indican a brown powder, from which he isolated six distinct substances, viz. *indihumin*, *indifuscin*, and *indiretin*, soluble in warm sodium hydroxide solution, and *α-* and *β-indifulvins* and *indirubin*, insoluble in alkalis.

When aqueous solutions of the indican were boiled or heated for some time a decomposition ensued, and the product, on treatment with acid, gave indiglucin, but no indigotin, this being replaced by *indiretin* and *indihumin*, brown amorphous substances. The latter closely resembled, and was probably identical with, indigo brown. By the action of alkalis or alkaline earths at the ordinary temperature, indican was converted into a new glucoside, *indicanin*, $C_{20}H_{23}NO_{12}$, which on treatment with acid gave indiglucin and indirubin.

Oxyindicanin, a brown gummy substance, insoluble in alcohol, was isolated during the preparation of indican, and yielded, under the influence of acids, indiglucin and a brown substance similar to indifuscin.

In 1896 Surg. Lt.-Col. G. S. A. Ranking (Jour. Asiatic Society of Bengal, lxv., ii., No. 1), as the result of a careful examination of the fermented leaf extract, pointed out for the first time that the soluble compound present and which by air oxidation gives indigotin, cannot be indigo white, but is evidently *indoxyl*. He also suggested that as CO_2 is largely evolved during the leaf fermentation it is not improbable that *indoxylic acid*,



may also be present.

Marchlewski and Radcliffe (J. Soc. Chem. Ind., 1898, 17, 434), evidently unaware of Ranking's paper, and indeed this seems to have been lost sight of by later workers, in a theoretical discussion of the subject, suggested that indican, $C_{14}H_{17}O_6N$, was a glucoside of indoxyl, the hydrolysis of which could be represented by the following equation :—

$$C_{14}H_{17}O_6N + H_2O = C_8H_7ON + C_6H_{12}O_6$$

As a result of the communication of Marchlewski and Radcliffe, Hazewinkel, the director of the experimental station for indigo, Klaten, Java (Proc. K. Akad. Wetensch., Amsterdam, 1900, 2, 512), gave an account of a research, concluded in 1898, which he had hitherto considered to be to the interest of the Java planters to keep secret. In this important paper he shows that indican is an indoxyl glucoside, and that the sugar obtained from it is dextrose.

The elaborate researches of Beyerinck, van Romburgh, and other Dutch chemists proved that the indican present in the various *Indigoferæ* and in the *Polygonum tinctorium* was far more stable than Schunck supposed, and the experiments of these authors eventually led to the isolation of this glucoside, in a crystalline condition from the *Indigofera leptostachya* and *Polygonum tinctorium* by Hoogewerff and ter Meulen (Proc. K. Akad. Wetensch., Amsterdam, 1900, 2, 520).

The leaves were immersed in two and a half times their weight of boiling water, boiled for a few minutes, and further systematically exhausted. Without any sensible decomposition the decoction could be evaporated *in vacuo* if care was taken to keep the reaction alkaline. The dry residue was extracted with methyl alcohol, and to the solution ether was added as long as a precipitate was formed. This was removed, the clear liquid evaporated, the residue completely dried *in vacuo*, and then dissolved in water. The filtered and concentrated solution deposited on cooling well-defined crystals of indican. This process may be modified by treating the decoction of the leaves with baryta water before concentration, by which means a large proportion of the impurities are precipitated. Seventeen kilos of the leaves of *Polygonum tinctorium* yielded 5 grams of pure indican.

Thus obtained indican, $C_{14}H_{17}O_6N$, crystallises from water in spear-shaped crystals, which contain 3 molecules of water of crystallisation. Heated in a test tube, or on platinum foil, purple-coloured fumes are given off, but this does not take place in an atmosphere of carbon dioxide. By passing a current of air through a hot solution of indican in dilute hydrochloric acid containing a little ferric

chloride, 91 per cent. of the indican was converted into indigotin according to the equation—

$$2C_{14}H_{17}NO_6 + O_2 = C_{16}H_{10}N_2O_2 + 2C_6H_{12}O_6$$

There was no difference between the indican prepared from the *I. leptostachya* and that obtained from the *P. tinctorium*.

In a paper by Beyerinck (Proc. K. Akad. Wetensch., Amsterdam, 1900, 3, 102), "On the Formation of Indigo from Woad," this chemist discusses Schunck's well-known work on the same subject, and points out that the indigo yielding substance contained in this plant is not, as Schunck regarded it, identical with the indican present in the *Polygonum tinctorium*. The colouring principle of woad Beyerinck names *isatan*, and shows that this compound, unlike indican, is decomposed in feebly alkaline solutions, whereas indican is stable even in concentrated alkaline liquids. In presence of acids both isatan and indican are hydrolysed, but indican with greater difficulty. *Isatase*, the specific enzyme of woad, does not act on indican, and isatan, on the other hand, is unaffected both by the indigo enzyme or by common bacteria.

Schunck (Chem. News, 1900, 82, 176) considered that the crystalline indican of Hoogewerff and ter Meulen was not the substance obtained by him, and should not be considered as a pure variety of it, but was rather derived from it, by extracting the plant with a hot solvent and the use of chemicals. He preferred to name his compound *a*-indican and theirs *b*-indican.

Bergtheil (Chem. Soc. Trans., 1904, 85, 877), who experimented with the *I. sumatrana* and *I. arrecta*, did not find it possible to prepare indican from the leaves of these plants in the manner described by Hoogewerff and ter Meulen.

It was, however, shown by Perkin and Bloxam (Chem. Soc. Trans., 1907, 91, 1715) that crystalline indican can be isolated from both of these plants by such a method, and is in reality the source of the natural indigo which is derived from them.

In a further communication ter Meulen (Rec. trav. chim., 1905, 29, 444) describes a modification of the method previously given for the isolation of indican from the *Polygonum tinctorium*, which consists in treating a cold solution of the partially purified substance with sulphuric acid, by which means certain impurities are precipitated. The acid is then removed with barium carbonate. The main object of the investigation was, however, the determination of the sugar that this glucoside yields when hydrolysed by its specific enzyme, and this proved to be dextrose, as already indicated by Hazewinkel (*loc. cit.*)

As a result of the study of the behaviour of indican with solvents, Perkin and Bloxam (*loc. cit.*) devised a very simple process for the isolation of this glucoside, by the aid of which large quantities of the pure substance could be readily prepared.

The leaves and stems of the *I. sumatrana* (1000 grams) were treated with 4 litres of cold acetone, the mixture being occasionally shaken during seven days, and the green-coloured extract was evaporated on the steam-bath to a very small bulk. To the residue light petroleum was added, causing the deposition of a brown viscous precipitate of crude indican, and this was repeatedly agitated with small quantities of light petroleum. The product on treatment with water gave a pale yellow liquid, containing resinous matter in suspension, and the latter was removed by shaking with ether. The clear aqueous solution, treated with 10 c.c. N/2 sodium carbonate, on gradual evaporation *in vacuo* deposited crystals, and eventually a semi-solid mass was obtained. It was collected, drained, and allowed to dry at the ordinary temperature. When exhaustively extracted, 1000 grams of leaf gave 31·66 grams of indican, and by a continuous system of working more than 500 grams of crystalline indican were prepared. The preparation of this glucoside from the leaves of *I. arrecta* is more troublesome, owing partly to the presence of kaempferitrin (*loc. cit.*), but more especially of a colourless sugar-like compound, $C_6H_{12}O_5$; melting-point 186—187°; possibly a modification of quercitol. The fact that indican can be so readily isolated without the aid of heat, and merely with the use of acetone, light petroleum and ether, is not in harmony with the contention of Schunck (*loc. cit.*) that the crystalline glucoside is an alteration product of his amorphous substance, and consequently the terms α- and β-indican suggested by him should disappear.

Indican crystallised from water, $C_{14}H_{17}O_6N$, $3H_2O$, melts at 57—58°, but in the anhydrous condition as obtained by the addition of boiling benzene to its hot alcoholic solution, at 176—178°. Owing to its somewhat ready solubility in water it can be more economically purified by the latter process, and, according to Perkin and Thomas (Chem. Soc. Trans., 1909, 95, 793), crystallisation from absolute alcohol gives excellent results.

It has been shown by Baeyer (Ber., 1881, 14, 1745) that indoxyl readily condenses with aldehydes and ketones to form the so-called *indogenides*, and Hazewinkel (*loc. cit.*) partly identified this substance by means of its condensation products with isatin, benzaldehyde, and pyruvic acid, relying, however, on their qualitative reactions, as he did not prepare these compounds in a pure enough condition

for analysis. Almost simultaneously Beyerinck (Proc. K. Akad. Wetensch., Amsterdam, 1899, 2, 120) prepared indirubin by hydrolysing crude indican in the presence of isatin.

Perkin and Bloxam (*loc. cit.*) and Gaunt, Thomas, and Bloxam (J. Soc. Chem. Ind., 1907, 26, 1174), who experimented with the pure substance, found that when indican dissolved in water is added to a boiling solution of isatin, acidified with a little hydrochloric acid, and the operation is carried out in an atmosphere of hydrogen or carbon dioxide, the yield of indirubin is quantitative according to the following equations:—

$$C_{14}H_{17}O_6N + H_2O = C_8H_7NO + C_6H_{12}O_6$$
$$C_8H_7NO + C_8H_5NO_2 = C_{16}H_{10}N_2O_2 + H_2O$$

This "isatin" method, for details of which see page 513, affords a ready means, not only for the analysis of the crystalline glucoside, but also for the estimation of the amount which is present in aqueous infusions of the leaf (*v. infra*).

More recently Perkin and Thomas (Chem. Soc. Trans., 1909, 95, 795), who studied in a similar way the condensation of indoxyl derived from indican with *p*-nitrobenzaldehyde, found that the *p*-nitrobenzaldehydeindogenide is deposited in quantitative amount, and that this reaction could also be employed for the analysis, both of crystalline indican and of that present in the leaf extract. The reaction takes place with extreme readiness, for with indican solution at a dilution of 1 in 1000, the above compound quickly separates, and even at 1 in 10,000 the condensation can be observed to take place. Piperonal and indican in the presence of dilute acid yield the analogous compound $C_{16}H_{11}O_3N$, orange-coloured needles, melting-point 223—224°; but this process, under analytical conditions, gave only approximately satisfactory results. As a side issue, *p*-hydroxybenzaldehydeindogenide, $C_{15}H_{11}O_2N$, orange-red needles, melting-point 267—269°, and dihydroxybenzaldehydeindogenide, $C_{15}H_{11}O_3N$, orange-red needles, melting-point 264—265°, were prepared from indican. The latter compound derived from protocatechuic aldehyde dissolves in concentrated sodium hydroxide, with a bluish-violet coloration, and dyes with mordanted woollen cloth well-defined shades.

On the other hand, when indican is hydrolysed with acid in the presence of an oxidising agent it does not appear possible to obtain a quantitative yield of indigotin. Hazewinkel (*loc. cit.*) states, in regard to this point, that acid oxidising agents convert indican into indigo, and this in turn is oxidised by an excess of the reagent. By

the use of ferric chloride and hydrochloric acid, Hoogewerff and ter Meulen obtained from the pure glucoside only 91 per cent. of the theoretical quantity of colouring matter, which appeared to contain indirubin, and was of doubtful purity. Gaunt, Thomas, and Bloxam (*loc. cit.*), who examined the behaviour of ammonium persulphate, a reagent suggested by Rawson for the analysis of the plant extract (Report on the Cultivation and Manufacture of Indigo, Mozzufferpore, 1904; cf. also Bloxam and Leake, Dalsingh Serai Report, 1904), found that the process was far from quantitative with pure indican, and that the yield of colouring matter averaged but 82 per cent. of the theoretical. Perkin and Thomas (*loc. cit.*) studied the effect of the hydrolysis of solutions of indican with acid during the aspiration of air through the liquid, under varying conditions of temperature and concentration. The most satisfactory yield of pure colouring matter (93·5 per cent.) was produced when air was passed during eight hours through a solution of 0·5 gram of the glucoside in 850 c.c. of water acidified with 15 c.c. of 33 per cent. hydrochloric acid, and the temperature maintained at 60°.

When, however, the operation was carried out at 70° less colouring matter was obtained (87·6 per cent.), and, curiously enough, replacement of the hydrochloric acid by an equivalent amount of sulphuric acid gave, under similar conditions, a much lower result. The deficiency in the yields given by these air-oxidation processes was due to the fact that a portion of the indoxyl had been converted into substances other than indigotin, and it was observed that whereas in the case of hydrochloric acid the filtrate possessed a pale yellow colour, that containing sulphuric acid had a browner and darker tint. Indirubin was also present in these indigo preparations.

Whereas Schunck (*loc. cit.*) had described the production of various brown substances by the action of dilute acids on his indican, and Schunck and Roemer (*loc. cit.*) had obtained a brown-yellow compound by means of hydrochloric acid in absence of air, the behaviour of the pure crystalline glucoside in this respect was studied by Perkin and Bloxam. When 100 c.c. of a 4 per cent. solution of indican was treated with 3 c.c. of sulphuric acid, and digested at a boiling temperature, the liquid, at first yellow, became brown, a brown resinous substance, together with a little indigotin, quickly separated, and the presence of indole was observed. The product of the reaction was almost identical in weight with that required by the amount of indoxyl which the glucoside would yield on hydrolysis, and consisted chiefly of a dark reddish-brown powder (*a*), sparingly

soluble in alcohol, together with a small quantity of a similar, though more readily soluble substance (*b*).* Analyses of (*a*), which is termed *indoxyl brown*, gave C = 68·10; H = 4·10; N = 9·34, figures almost identical with those found by the same authors for the main constituent of indigo brown, and though these two products differed from one another in certain minor respects, there could be no doubt that they were closely allied. The more readily soluble substance (*b*) also closely resembled the indoxyl brown, and gave on analysis N = 9·65 per cent. Indican, when treated with cold hydrochloric acid in the absence of air for ninety hours, gave indoxyl brown and a soluble brown substance similar to that described above (Perkin and Thomas). The acid filtrates from the indoxyl brown preparations contained dextrose, and this was identified by means of its osazone, and also by the preparation of its acetyl derivative.

The *indigo enzyme* discovered by Schunck (*loc. cit.*) has been elaborately investigated by the Dutch chemists. Beyerinck (Proc. K. Akad. Wetensch., Amsterdam, 1899, 1, 120) extracts the finely divided leaves of the plant, first with cold 96 per cent. alcohol, and subsequently with more dilute alcohol, which removes chlorophyll, indican, wax, etc., and leaves a snow-white highly active powder. From such preparations the enzyme itself could only be imperfectly removed, for in water it is almost insoluble, very sparingly so in glycerol, and rather more readily in 10 per cent. solutions of sodium and calcium chlorides respectively. The residue which remains after extraction in this way is not perceptibly less active than before treatment. A minute study of these leaf preparations was carried out by Beyerinck in regard to their behaviour with partly purified indican solutions, and he indicates the effect of temperature on the intensity of the hydrolysis by means of curves. Among numerous points of interest it was observed that ammonia quickly destroys the enzyme, and also that emulsin slowly hydrolyses indican, although the intensity of its action was only one-twentieth of that of *Indigofera* enzyme preparations.

Hazewinkel (*ibid.*, 1900, 2, 513), who also investigated the subject in 1898, arrived independently at Beyerinck's conclusions. Finding that emulsin acted on indican solutions he called the indican enzyme *indimulsin*, and considered that a 10 per cent. solution of sodium chloride is the best medium for dissolving it. A very

* According to Perkin (Chem. Soc. Trans., 1916, 109, 211) this operation can be so conducted that the total amount of nitrogen present in this product is approximately equivalent to that possessed by the indican originally employed.

interesting point which he mentions is that during fermentation no indican passes from the leaf into the surrounding liquid.

In the paper of van Romburgh (*ibid.*, 1899, 2, 344) allusion again is made to the insoluble character of the enzyme, and to the activity of emulsin with solutions of indican. Finally, Beyerinck (*ibid.*, 1900, 3, 101) demonstrated that the ferment present in woad, *Isatis tinctoria*, is not capable of hydrolysing indican, though it reacts with isatan, the peculiar indigotin yielding principle of this plant. Bergtheil (Chem. Soc. Trans., 1904, 85, 877), whose paper covers ground already traversed by Hazewinkel, Beyerinck, and van Romburgh, considers that the difficulty which occurs in extracting the enzyme is due to the presence of tannin in the leaves (cf. Brown and Morris, Chem. Soc. Trans., 1893, 63, 604). By pounding the leaves with hide powder the tannin becomes fixed, and a very active solution of the enzyme can be obtained.

Ter Meulen (Rec. trav. chim., 1905, 24, 444) is, however, in agreement with the other Dutch work referred to above, as is evident from his statement "L'enzyme de l'indigo est insoluble dans l'eau". According to Gaunt, Thomas, and Bloxam (*loc. cit.*), Bergtheil's product is not a true solution, as the enzyme is entirely removed from it by means of a Berkfeld filter. Thomas, Perkin, and Bloxam (Chem. Soc. Trans., 1909, 95, 829), again, point out that there is no certainty of the presence of tannin in the leaves of the *I. sumatrana* and *I. arrecta*, and that any tannin matter if originally present would be eliminated during the repeated extraction of the material with alcohol. As the result of their experiments the insolubility of the enzyme was confirmed.

A study of the hydrolysis of pure indican by means of the enzyme and subsequent oxidation of the indoxyl solution with air under varied conditions has been made by Thomas, Perkin, and Bloxam (*loc. cit.*). The fermentation was carried out in an atmosphere of purified hydrogen, and the temperature and dilution of the solution in both this and the subsequent oxidation process were so arranged as to fairly approximate the ordinary factory routine. For full details of apparatus and the analytical precautions adopted the original paper must be consulted.

The results of this investigation show that the hydrolytic action of the enzyme proceeds somewhat rapidly, and that by employing 2 grams of the enzyme and 1 gram of indican under the conditions of dilution stated, the reaction was complete after 2 hours' digestion at 50°. The solution, though free from indican, contains, however, less than the theoretical amount of indoxyl (93 per cent.). This is due

to the fact that some quantity of the indoxyl (4 per cent.) is occluded by the enzyme powder, and it was found that by increasing the quantity of this latter a correspondingly greater loss occurs. The residual deficiency (3 per cent. approx.) arises from the instability of indoxyl itself, which even in an atmosphere of hydrogen at 50° is slowly converted into a product which is incapable of giving indigotin on oxidation. This property, which is referred to as the "decay" of indoxyl, is much more evident when the digestion with the ferment is prolonged for several hours, and the experiments of these authors indicate that by such a treatment for 30 hours, at least 20 per cent. of the indoxyl undergoes this transformation. On the other hand, at 15°, in an atmosphere of hydrogen, the indoxyl solution is comparatively stable, and on standing for 24 hours, experienced a loss of only 3 per cent.

According to Beyerinck (*loc. cit.*) great attention should be paid to the degree of the acidity of indican solutions which are undergoing fermentation, and this is corroborated by Thomas, Perkin, and Bloxam. Thus, by the presence of a trace of sulphuric acid, during the fermentation, the decay of the indoxyl is practically inhibited, and, moreover, by the addition of a further quantity of the acid at the close of the operation, the occlusion of the indoxyl by the enzyme powder is also prevented. As a result of this procedure the solution contained 99·5 per cent. of the theoretical quantity of indoxyl.

When a dilute aqueous solution of indoxyl is oxidised by air the reaction is more complex than has usually been considered the case, and a quantitative yield of indigotin is not produced. Thomas, Perkin, and Bloxam have, for instance, found that the indoxyl solutions produced by the enzyme hydrolysis of indican, when treated with air at 60°, gave only 88 per cent. of the theoretical quantity of indigotin, admixed with a little indirubin. It thus appears evident that in addition to the oxidation of indoxyl to indigotin some secondary reaction occurs, but of the chemical nature of this change there is as yet no certain evidence. The isolation from the indigo thus produced of traces of substances resembling indoxyl brown or indigo brown indicates the effect, at least in part, of a condensation similar in character to that which is involved in the production of the former product. Moreover, the filtrate from the indigo, which is prepared in this manner, was invariably of a dull yellow colour, and yielded, by extraction with ether, a small quantity of a yellowish-brown resin.

This secondary change of indoxyl is facilitated by the presence of potassium acetate in the liquid during the oxidation, for by this

means the yield of indigotin was decreased to 81 per cent., and the filtrate obtained from it possessed a rich dichromate colour. It has long been known that the oxidation of indoxyl solutions, in so far as the crude fermented factory liquid is concerned, is facilitated by the presence of ammonia or lime water, and the subject has been discussed by Rawson and by Beyerinck (*loc. cit.*). According to Thomas, Perkin, and Bloxam, the employment of a small quantity of either of these reagents during the oxidation of the indoxyl derived from pure indican was beneficial, and an increase of about 5 per cent. in the yield of indigo thus took place. On the other hand, the addition of only a trace of these compounds is advisable, because should an excess be present the amount of indigo produced is rather decreased than increased thereby.

But whilst both ammonia and lime water in suitable amount partially inhibit the secondary change of the indoxyl referred to above, a third factor, well known to manufacturers, comes into play, which is represented by the production of notable amounts of indirubin. For the formation of this colouring matter isatin is necessary, and it is likely that, in the presence of a large amount of the above reagents, an excessive production of this substance occurs, and occasions the decreased yield of indigo which, under these circumstances, has been shown to take place. It has, in fact, been pointed out by Perkin (Chem. Soc. Proc., 1907, 23, 30) that traces of isatin exist in Java indigos, which are rich in indirubin.

Curiously enough the presence of a trace of hydrochloric acid during the oxidation acts in the same manner as ammonia, though to a less extent, in increasing the yield of colouring matter, but in this case the reaction proceeds much less rapidly. The employment of pure oxygen with neutral solutions of indoxyl gives 3—4 per cent. less colouring matter than is obtained when air alone is employed, whereas in presence of ammonia the yield is but little affected. The addition of Chile saltpetre to the fermentation vat has been a custom of Indian planters for some time, and Rawson (Report on the Cultivation and Manufacture of Indigo, 2nd ed., 1907) states that although no increase of colouring matter is thus produced in the oxidation vat, the precipitate settles better. The laboratory experiments of Thomas, Bloxam, and Perkin with pure indican corroborate this statement. Finally, there is but little difference in the yield of colouring matter experienced when the solution of indoxyl is oxidised by air at either 30 or 60°, although, if anything, the advantage is in the case of the higher temperature.

As a result, therefore, of the employment of acid during the

enzyme hydrolysis of indican, and oxidation of the resulting indoxyl solution under feebly alkaline conditions, the best yields of colouring matter have been obtained. On the other hand, it has not been found possible either with synthetical indoxyl or indoxyl derived from indican to obtain a quantitative yield of pure indigotin or of an admixture of this colouring matter with indirubin. In regard to the bearing of this work on the commercial process, Thomas, Perkin, and Bloxam suggest that the effect of the addition of a small quantity of sulphuric or oxalic acid to the fermentation vat should be studied. They consider, however, that the most satisfactory laboratory results on the preparation of indigotin from the plant extract, or from pure indican, are given when the solution is hydrolysed by hydrochloric acid, with simultaneous oxidation by air. The cost of hot water extraction of the plant is, however, considered by Rawson to be prohibitive.

Bacterial Fermentation.—Though in the manufacture of indigo, hydrolysis of the indican is mainly due to the action of its specific enzyme indimulsin, it is well known that the bacteria which are present exert a similar although minor effect.

In 1887 Alvarez (Compt. rend., 115, 286) isolated from an extract of the indigo plant, an organism *Bacillus indigogenus*, which was capable of producing this fermentation. Beyerinck (*loc. cit.*) who studied the matter in considerable detail, points out that a similar effect is produced by infecting indigo plant infusions with garden soil, and that in this case the common gas-producing bacteria perform the chief part. Alvarez, he suggests, went too far in insisting on the existence of a specific bacterium in indigo fermentation. On the other hand, Bergtheil (*loc. cit.*) considers that at least one organism capable of producing indigo fermentation is invariably found in large quantities in an infusion of the plant. This corresponds very closely with the description given by Alvarez of his *Bacillus indigogenus*, and is no doubt identical with it.

Manufacture of Indigo.

Water.—Pure water in large quantity is necessary for the manufacture of natural indigo (Crookes, "Handbook of Dyeing and Calico Printing," 1874; "Indigo Manufacture," Bridges-Lee, 1892; Rawson, Report on the Cultivation and Manufacture of Indigo, 1902). When such is not available, Bridges-Lee recommends its purification, if hard, by treatment with lime water, and should much organic matter be present by the use of permanganate. Rawson

also lays stress on this point, and recommends a similar method of procedure. In special circumstances the employment of alumino-ferric is advisable (Bergtheil, 1909). As the duration of the fermentation varies with the temperature of the water, Rawson recommends, in case this should be lower than 90° F., a preliminary heating in the reservoir.

Fermentation.—The duration of this process is given by Crookes (*loc. cit.*) as nine to fourteen hours, according to the prevailing temperature of the water, whereas Georgievics (Der Indigo, 1892) suggests eighteen hours when the external temperature is 35·6° C. In very hot weather the fermentation is completed in six hours. According to Rawson (*loc. cit.*) when the temperature of the fermentation vat is from 90—92° F. a twelve hours' steeping gives the best result in the case of the *I. sumatrana;* whereas Bergtheil (Indigo Research Station, Sirsiah, 1906) is of opinion that a ten hours' fermentation is sufficient. With the *I. arrecta* the steeping should vary from thirteen to fifteen hours at 90°, according to the indican content of the plant. In other respects, according to Rawson and Bergtheil, there is practically no improvement necessary in the steeping operation as carried out in well-managed factories. The addition of such chemicals as mercuric chloride, sodium and potassium carbonates, lime, carbolic acid, formaldehyde, and sugar are not of advantage, although sodium nitrate, which has been employed by planters for many years past, may facilitate the deposition of the indigo in the oxidising vat. On the other hand, the work of Thomas, Bloxam, and Perkin indicates as beneficial the curtailment, as far as possible, of the steeping operation, and the addition of sulphuric or oxalic acid in small quantity to the vat as advantageous.

Hot-water Extraction.—The extraction of the indigo plant with hot water has been employed for many years, and in Bancroft's "Philosophy of Permanent Colours" an account is given by Dr. Roxburgh, dated 1797, of such a method:—

"The hot-water process begins to be used over these provinces . . . with it they can make indigo when the weather is too cold for the usual process of fermentation, and it gives a more beautiful and lighter indigo. . . . A more complete and certain extraction of the basis of indigo is effected by subjecting the plant to the action of water heated to about 150—160° F." Bridges-Lee (*loc. cit.*) claims an advantage by the employment of hot water, and heats the contents of the steeping vat gradually, either by direct fire or steam pipes. It is also well known that the Java planters who have employed the *I. arrecta* for several years past have favoured a hot-

water process, and although the exact details of their methods have not been disclosed, it is certain that sulphuric acid is also employed in the manufacture. Perkin (Chem. Soc. Trans., 1907, 91, 435) refers to samples of Java indigo prepared by three distinct methods, viz. "the new process with hot water," "the new process with cold water," and "the old process in which no chemicals are used". There can be no doubt that by these hot-water processes the indican is very rapidly hydrolysed by the ferment, and that the indigo eventually produced is of a superior quality. During this hot extraction it appears preferable, as far as possible, to exclude air from the vat by means of a cover, and the necessity in this case is easy to understand because the evolution of carbon dioxide and other gases which act as a protection to the indoxyl during the ordinary process of fermentation, is greatly decreased when operating in this manner (Roxburgh, *loc. cit.*). Rawson (*loc. cit.*) who refers to a patent No. 157, 1892, granted to A. Schulte in Hofe, for manufacturing indigo on these lines, and also to Henly's "heating process of 1888," carried out numerous experiments on this subject with the *I. sumatrana*. In order to economise fuel the indigo plant was, in the first instance, extracted by the accumulative method; but, contrary to expectation, this did not give such good results as a simple extraction in ordinary vats fitted with perforated steam pipes. He finally concludes, however, that except in wet or cold weather the hot-water system offers no advantage over ordinary steeping carried out under favourable conditions. The indigo made by this method was, however, of better quality (75—77 per cent.) than that made in the ordinary way (50—55 per cent.). In regard to extraction of the plant by means of boiling water, or extraction by steaming, Rawson considers that the cost would be prohibitive.

When the fermented liquid is run into the oxidising vat, the residual plant still contains a small quantity of indoxyl. The question of a second steeping in order to recover this is referred to by Roxburgh as early as about 1797; he considers that a considerable economy would probably be effected thereby; but Rawson's (*loc. cit.*) experiments in this direction gave an unsuccessful result. Thomas, Perkin, and Bloxam (*loc. cit.*) suggest that the employment of a slightly acid water for this purpose should be advantageous, and that the amount of indoxyl retained by the plant residue is probably greater than the 5 per cent. (on the total colouring matter) believed by Rawson to be present. The extracted plant, known as "seet," is a valuable manure.

The Oxidation Vat.—Although the oxidation of the fermented

liquid was until very recently carried out to some extent by "hand beating," a method practised over a century ago, according to Bancroft (*loc. cit.*), this operation is commonly effected by machinery. The apparatus is identical with, or very similar to, the "beating wheel," a rimless wheel, the spokes of which are paddles, and which is now very generally employed in India. Geneste in 1888 patented the pumping in of air, and Bridges-Lee (*loc. cit.*) in 1891 a shower-bath arrangement, as improvements in the method of oxidation. Rawson, again (1902, Eng. Pat., 173), proposed to treat the liquid with acid and an alkaline persulphate; but although excellent results were obtained in the laboratory, these were not satisfactory on the manufacturing scale. As the outcome of an elaborate investigation, Rawson considers that the oxidation of the fermented liquid by blowers and compressors is superior to wheel beating, the yield being thereby increased about 20 per cent.

It has long been the custom to facilitate the deposition of the indigo by what were termed "precipitants," and experiments are recorded by Roxburgh, who employed for this purpose ammonia, stale urine, caustic lye, lime-water, and potassium ferrocyanide. That such chemicals must be considered to have assisted in the more rapid oxidation of the indoxyl is certain, and their effect is not to be confused with the mere settlement of the indigo by the use of slaked lime, as adopted by the Chinese.

In 1894 Coventry patented a process which was based on the employment of lime under certain conditions. The invention consisted in the employment of a special vat intermediate between the steeping and oxidising vats, in which the fermented liquid was treated with lime. A copious precipitate of calcium and magnesium carbonates was thus produced, which on settling carried down various impurities. The supernatant liquid was then oxidised in the usual manner. The indigo thus produced is somewhat contaminated with lime, and the removal of this is subsequently effected by the addition of a certain amount of acid to the "mal" in the boiler. Indigo prepared in this manner is of superior quality, and although not equal to the Java product resembles the latter in containing some quantity of indirubin. According to Rawson a substantially increased yield of colouring matter is given by this process.

Caustic soda added to indigo-liquor before oxidising behaves very similarly to lime, and on the large scale gave an increase of 43 per cent. of dry indigo as weighed. Sodium peroxide also gave an average increase of 33 per cent., but on the whole was not so serviceable as caustic soda (Rawson).

The oxidation of the fermented plant extract in the presence of ammonia, first mentioned by Roxburgh (*loc. cit.*), was patented by Michea in 1876, whereas Geneste in 1889 suggested the use of caustic soda and ammonium sulphate instead of liquid ammonia itself. The use of ammonia is mentioned as beneficial by Georgievics (*loc. cit.*), and there appears to be no doubt that it is superior to the other reagents which have been employed for this purpose. In its presence the indoxyl is rapidly oxidised to indigotin, and the precipitated colouring matter settles well. The more general employment of ammonia in India has resulted from the work of Rawson, and its use in conjunction with the steam injector blower constitutes the most important improvement which he has recommended to the notice of the indigo planters. The procedure adopted by Rawson consists briefly in connecting the outlet of an ammonia still (containing lime and ammonium sulphate) loosely with the steam blower, so that when in action, ammonia, air, and steam are injected into the vat by means of perforated pipes laid at the bottom of the receptacle. During the operation the temperature rises 10—15° F., and the oxidation is rapidly completed. The employment of ammonia gas and steam in connection with the beating wheel gives also satisfactory results. By these methods Rawson describes increases in the yields of dry indigo, varying from 37—63·8 per cent., and considers that the average increase of colouring matter is about 34 per cent. as compared with that given by the ordinary oxidising process.

On the other hand, Bergtheil (Report of the Indigo Research Station, Sirsiah, 1906, 6) states that the ammonia process effects very little, if any, improvement over ordinary oxidising when this is carried out under optimum conditions of speed, weather, etc.

After the indigo has settled in the vat, the supernatant liquid, or "seeth" water, is run off as completely as possible. This seeth water, as a rule, contains more or less colouring matter in suspension, and it is during this operation that a considerable loss of indigo occurs, which may reach as much as 20 per cent. (Rawson). This, as a rule, is much reduced by using an alkali in oxidising, on account of the readier settlement of the precipitate. Rawson found that filter pressing cannot be employed for recovering the indigo, but suggests treating the "seeth" water with an alkali which causes the suspended indigo to more readily subside. On the other hand, Bergtheil (1909) recommends the employment of alumino-ferric as an aid to the deposition of the indigo precipitate in the oxidation vat.

Final Treatment of Indigo.—According to Bancroft (*loc. cit.*) it was the practice of some manufacturers in the East Indies to purify

their indigo by boiling it with water and fossil alkali (soda), whereas Roxburgh, as well as de Cosigny, recommended also the action of a diluted sulphuric acid. The more general procedure, until very recently, in India has consisted in merely boiling the semi-fluid indigo paste in a large cauldron, but the addition of dilute sulphuric acid appears now to be generally adopted. According to Rawson the quality of the indigo may be in this way improved 5—10 per cent. At the close of the operation the indigo is allowed to settle, the acid liquid run off, and the precipitate treated with fresh water and again boiled.

The subsequent filtering, pressing, and drying operations call for no special comment. The slow drying of the product appears to be most advantageous, and in this way an indigo of slightly higher percentage than when the mass is dried artificially is obtained. This is accounted for by the fact that certain impurities of the indigo in the presence of moisture undergo gradual decomposition with evolution of ammonia and other gases.

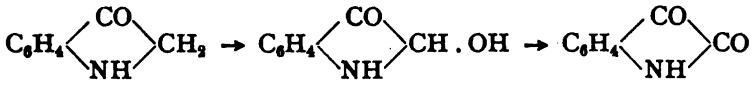
Briggs (Pat. Spec. 292, 1906) devised an apparatus for drying the indigo paste, and simultaneously converting it into powder. An illustration of this machine, essentially a revolving drum, appears in Bergtheil's Report, 1906, 12. Attempts, moreover, are being made to place natural indigo on the market in the paste form (*ibid.*, 1910).

Constituents of Natural Indigo.

In addition to indigotin, natural indigo contains varying proportions of indirubin, indigo brown, indigo gluten, and mineral matter. Indigo yellow or kaempferol is also present as a rule when the *I. arrecta* has been employed for the manufacture.

Indirubin.—The identity of the natural indirubin or indigo red with the artificial product prepared according to Baeyer's method (*loc. cit.*), about which there was formerly some controversy, appears now to be fully established (Marchlewski and Radcliffe, J. Soc. Chem. Ind., 1898, 17, 434). Bloxam at one time (Chem. Soc. Trans., 1905, 87, 979) considered that a red substance other than indirubin was present in some quantity in natural indigo, whereas Bergtheil (Report of the Indigo Research Station, Sirsiah, 1906) has stated that "decisively there is more than one red body in most commercial indigos". The investigation of numerous samples of the dyestuff by Perkin and Bloxam (Chem. Soc. Trans., 1907, 91, 279, and 1910, 97, 1461) indicate, however, that this is not the case. Whereas certain varieties of natural indigo, notably Java and

Coventry process indigos, contain notable amounts of indirubin, it is probable that a trace occurs in all samples of the natural dyestuff. That the indirubin originates from the indican existing in the leaves of the various species of *Indigofera*, and is due to no second constituent of the plant, is now certain, and its production is to be explained in all cases as due to the condensation of isatin with indoxyl. Thus it has been shown by Thomas, Bloxam, and Perkin (*loc. cit.*) that indigo containing indirubin can be readily produced from indican by a repetition of the factory method, and again, isatin itself has been isolated from natural indigo rich in indirubin (Perkin, Chem. Soc. Proc., 1907, 23, 30). The formation of the isatin is favoured by special circumstances such as the oxidation of the indoxyl by air in the presence of alkali or acid, and may also be affected to some extent by temperature. That indoxyl can be converted into isatin without an intermediate formation of indigotin has been shown by the Badische Anilin und Soda-Fabrik (D.R.P., 107719, 1898), and it has been found by Perkin (Chem. Soc. Trans., 1909, 85, 847) that indoxylic acid, on long standing in the presence of moist air, is converted chiefly into indirubin, although some quantity of indigotin together with a substance, probably indigo brown, and traces of isatin are simultaneously produced. Again, it has been pointed out (Thomas, Bloxam, and Perkin) that the indican present in air-dried leaves of the indigo plant slowly disappears, and, according to Perkin (private communication), this is accompanied in most cases by a development in the leaf of considerable quantities of indirubin. It appears probable that this so-called "secondary" oxidation of the indoxyl proceeds according to the following scheme:—



and may also be indirectly the cause of the production of indigo brown. The following are the results of analyses illustrating the percentages of indirubin and indigotin in certain indigos (Bloxam and Perkin):—

Java Indigo.—New process with hot water.

Sample.	Total Colouring Matter.	Indigotin.	Indirubin.
1.	75·20	67·76	7·43
2.	73·60	63·86	9·51
6.	62·91	57·35	5·01

Java Indigo.—New process with cold water.

Sample.	Total Colouring Matter.	Indigotin.	Indirubin.
7.	72·88	69·23	3·06
8.	71·02	66·35	4·04
9.	58·30	55·61	2·15

Java Indigo.—Old process without chemicals.

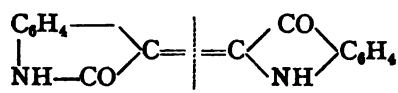
13.	74·96	72·89	1·74
15.	69·54	68·26	0·99

Coventry process indigo.

61·76	56·63	5·23

Finally, Bloxam and Perkin refer to an abnormal sample of laboratory indigo prepared from pure indican, which contained 88·9 per cent. of colouring matter, and of this 25·83 per cent. consisted of indirubin.

Though indirubin was at one time considered to be a valuable constituent of natural indigo (cf. Rawson and Knecht, J. Soc. Dyers, 1888, 4; Hummel, *ibid.*; and Bergtheil, Report Indigo Research Station, Sirsiah, 1907, 7), it is now known that such is not the case. Fasal (Mitt. K. Tech. Gew.-Mus. Wien, 1895, 11, 307) found that the shade of colour given by an indirubin vat became bluer from day to day, and that this was due to the formation of indoxyl by the further reduction of the leuco-indirubin. More recently Perkin (Chem. Soc. Proc., 1909, 25, 127) has shown that in addition to indoxyl, *oxindole* is simultaneously produced, and this is in harmony withrthe formula assigned by Baeyer (*loc. cit.*) to this substance—



In vat dyeing, therefore, indirubin may thus produce not more than one-half its weight of indigotin. Matthews (J. Soc. Chem. Ind., 1902, 21, 22), again, points out that indirubin requires for reduction a much stronger reagent than indigotin, and as a result, in practice, the greater part of this dyestuff is not attacked, but settles to the bottom of the vat.

On the other hand, indirubin disulphonic acid is, according to Fasal (*loc. cit.*) and also to Rawson and Knecht (*loc. cit.*), a useful dyestuff, and gives colours much faster to light than indigotin disulphonic acid, which is present as sodium salt in the "indigo extract" of commerce.

Indigo Brown.—An important impurity of natural indigo is the so-called indigo brown, a product isolated and cursorily examined by both Chevreul (Gmelin, Handbook of Chem., 1859, 13, 48) and Berzelius (*ibid.*). In order to isolate this substance, the latter chemist digested indigo with boiling dilute sulphuric acid to remove indigo gluten, and subsequently with potassium hydroxide to dissolve the brown. The alkaline liquid was neutralised with acetic acid, evaporated to dryness, the residue digested with alcohol, and the solution evaporated. Thus obtained the indigo brown consisted of a dark-coloured resin, soluble in alkaline solutions. According to Schunck (Phil. Mag., 1855, [iv.], 10, 74, and *ibid.*, 1858, 15, 127) the indibumin, $C_{10}H_9O_3N$, produced in conjunction with other brown amorphous products by the action of dilute acids on his indican is, perhaps, identical with indigo brown.

Perkin and Bloxam (Chem. Soc. Trans., 1907, 91, 279) extracted Bengal indigo, which had been already digested with boiling dilute hydrochloric acid to remove the gluten, with boiling pyridine. In addition to a little indirubin the product contained three substances: (*a*) the main constituent, $C_{16}H_{12}O_2N_2$ (?), insoluble in alcohol and acetic acid, (*b*) $C_{24}H_{22}O_5N_2$ (?), soluble in acetic acid, and (*c*) $C_{16}H_{14}O_4N_2$ (?), soluble in alcohol. These compounds, the molecular weight of which is uncertain, consist of brown amorphous powders, closely resembling one another in general property, and are readily reduced by zinc-dust in alkaline solution with formation of pale brown liquids. When digested with boiling 50 per cent. potassium hydroxide solution they give some quantity of *anthranilic acid*, a point which indicates that they are derived from indoxyl. At the same time a brown resinous substance is also produced, and this studied in the case of the main constituent (*a*) $C_{16}H_{12}O_2N_2$ contained C = 71·39; H = 4·05; N = 7·94. Natural indigo further contains a small quantity of a brown substance, insoluble in pyridine, but soluble in boiling dilute alkali (Chem. Soc. Trans., 1910, 97, 1473), and is distinguished from the compounds above enumerated by the fact that it is not susceptible to sulphonation (with 96 per cent. sulphuric acid) or conversion by this means into a product soluble in water. In the analytical method described by Rawson (J. Soc. Chem. Ind., 1899, 18, 251) this brown material, at least in part, consists of the impurity which is carried down by a precipitation of barium sulphate in the liquid. There is now considerable evidence in favour of the view that the constituents of indigo brown are derived from indoxyl during the manufacture of indigo from the plant. The fact that indican itself, when boiled

with dilute acids, produces the very similar indoxyl brown, and the isolation of brown substances, although in trifling amount, from indigo prepared by the hydrolysis of pure indican in the laboratory, harmonises with this suggestion.

Beyerinck (Proc. Roy. Akad. Scien. Amsterdam, 1899, 120) observed that the disappearance of indoxyl in a dyeing woad (*Isatis tinctoria*) leaf is accompanied by the appearance of brown substances. Again, he states that "strong acids, just as alkalis . . . favour the formation of indigo from indoxyl, but then part of this substance constantly changes into a brownish-black matter". It has also been noted by Thomas, Perkin, and Bloxam that the disappearance of indican in the leaves of the *I. sumatrana* on keeping is accompanied by the formation of brown extractive matter. Rawson, again (Report on the Cultivation and Manufacture of Indigo, Mozzufferpore, 1904), says, "The blower . . . by quickly getting rid of CO_2 gas . . . prevents decomposition of a portion of the colouring matter into worthless brown substances, which takes place to a greater extent under other conditions". All indigos, moreover, appear to contain indigo brown, so that this property is irrespective of their origin, which may have been due to such distinct plants as the *Indigoferæ*, the *Polygonum tinctorium*, or the *Lonchocarpus cyanescens* of West Africa. Finally, it has been shown by Perkin (*loc. cit.*) that among the decomposition products of commercial indoxylic acid which has been kept for a long time, a brown compound exists, which has a very similar percentage composition, and is probably identical with the main constituent of indigo brown. It is quite possible that indoxylic acid is produced during the fermentation process (Perkin), (*cf.* Ranking, *loc. cit.*), and may be concerned in the formation of this product. The percentage of indigo brown soluble in pyridine in natural indigos is very variable, and appears to depend upon the details of manufacture. Analyses made by Bloxam and Perkin (Chem. Soc. Trans., 1910, 97, 1472) gave the following result:—

Java indigo, new process, hot water.	*Java indigo, new process, cold water.*	*Java indigo, ordinary process.*	*Coventry process indigo.*	*New Bengal indigo.*
5·4	5·2	4·15	8·7	9·60

Except in the case of the Coventry process indigo, these samples had all been derived from the *I. arrecta*. The average amount of crude indigo brown—containing, however, some mineral matter—in numerous samples of Bengal indigo prepared from the *I. sumatrana* was 14 per cent. (Chem. Soc. Trans., 1907, 297).

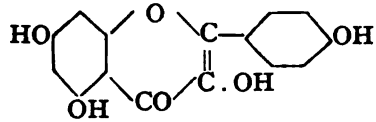
Indigo brown dissolved in alkaline hydrosulphite solution does not colour cotton fabrics, though woollen material dyed with natural indigo and stripped by the method of Green, Gardner, Frank, and Lloyd (*loc. cit.*) frequently possess a light brown tint which is probably due to the presence of this compound. The amount, however, remaining in this way on the fibre is not sufficient to materially strengthen the colour effect, and the frequently asserted superiority of the natural over the artificial variety of indigo can hardly therefore be accounted for in this manner.

Indigo Gluten.—Indigo gluten was first isolated from crude indigo by Berzelius (Berz. Jahresb., 7, 26) who extracted it with dilute acid, neutralised the extract with chalk, evaporated to dryness and dissolved out the gluten with alcohol. It was subsequently prepared by Orchardson, Wood, and Bloxam (J. Soc. Chem. Ind., 1907, 26, 4), who describe it as a horny mass, which on grinding gives a light biscuit-coloured powder, and when heated evolves ammonia. In cake indigo it appears to exist in combination with mineral matter, possibly as a calcium compound, for though itself readily soluble in water, it can only be removed from the dyestuff by means of dilute mineral acid. A considerable quantity of this substance is frequently present in indigo, and Perkin and Bloxam (*loc. cit.*) found that when the crude Bengal variety containing approximately 62 per cent. of indigotin was digested with dilute hydrochloric acid, it lost 21·5 per cent. of its weight. This figure naturally includes some quantity of mineral matter simultaneously removed by the acid. It has been suggested that this compound plays an important rôle in the dyeing operation, and accounts in part for the alleged superiority of natural over artificial indigo. This point, however, has not been scientifically investigated.

Indigo Yellow.—The first application of the term "Indigo yellow" to a substance existing in natural indigos is due to Bolley and Crinsoz (Jahres., 1866, 573) who state that it is to be found in the Bengal variety, and can be isolated by sublimation. It is described as golden-yellow needles, subliming at 130°, and soluble in soda lye. Crude Bengal indigo, however, gives no sublimate of this character (Perkin, Chem. Soc. Proc., 1906, 22, 198), but by submitting refined indigo, or the commercial synthetical variety to sublimation with limited access of air, a trace of a yellow compound, $C_{15}H_8O_2N_2$, is produced. This substance, however, is insoluble in alkaline solutions, and cannot, therefore, be the indigo yellow of Bolley and Crinsoz.

Rawson (J. Soc. Chem. Ind., 1899, 18, 251) detected in Java indigos a yellow compound, present usually to the extent of 2—3 per

cent., although in one special sample as much as about 20 per cent. occurred. This substance was soluble in alkalis with a yellow colour; on heating it partially sublimed, and had the properties of an adjective yellow dyestuff. A more recent investigation (Perkin, Chem. Soc. Proc., 1904, 20, 172) has indicated that this in reality is *kaempferol*—



a trihydroxyflavonol known to exist (Chem. Soc. Trans., 1902, 81, 587) in the flowers of the *Delphinium consolida* (Linn.) and other plants. Ultimately it was shown that the leaves of the *I. arrecta*, from which Java indigo is prepared, contain sometimes as much as 4 per cent. of a glucoside, *kaempferitrin*, $C_{27}H_{30}O_{14}$, almost colourless needles, melting-point 201—203°, which when digested with acid gives kaempferol and rhamnose—

$$C_{27}H_{30}O_{14} + 4H_2O = C_{15}H_{10}O_6 + 2C_6H_{12}O_5, H_2O$$

This compound is not hydrolysed by the indigo enzyme, and no enzyme has as yet been isolated from the plant possessing such a property. It is likely (Chem. Soc. Trans., 1907, 91, 435) that the use of sulphuric acid, when manufacturing Java indigo, may result in the contamination of the dyestuff with kaempferol. When the wet indigo sludge or "mal" is boiled in the "mal" boiler with addition of a little of the acid, the kaempferitrin present in the adhering water will be hydrolysed, and the insoluble colouring matter remain with the indigo. Samples of Java indigo more recently obtained contained only a trace (0·2 per cent. approx.) of kaempferol, whereas in a sample of the new Bengal indigo manufactured from the *I. arrecta* approximately the same quantity was detected (Perkin, private communication). If indigo mixed with kaempferol is cautiously sublimed the sublimate then contains appreciable quantities of this yellow colouring matter, and it seems likely, therefore, that this is in reality the indigo yellow of Bolley and Crinsoz, but that the indigo experimented with by these authors did not, as they supposed, originate from Bengal. The leaves of the *I. sumatrana*, the Indian indigo plant, contain but the merest trace of a yellow dyestuff resembling kaempferol, but according to Henry (Gmelin's Handbook of Chem., 1846, 13, 50) the *Polygonum tinctorium*, or Chinese indigo plant, contains appreciable quantities of a yellow colouring matter.

Seeth Water.

When "seeth" water, the liquid from which the indigo precipitate settles out at the conclusion of the oxidation process, is evaporated to dryness, yellowish-brown to deep brown residues are obtained. These products are extremely hygroscopic and when ground emit an odour resembling that of decayed cheese. Three samples of this material were examined by Perkin (Chem. Soc. Trans., 1916, 109, 211), the first and most important of which, derived from water drawn from an oxidation vat in the Purtabphore factory in India, represented 0·75 per cent. of the original liquid. As in the process of manufacture 100 parts of *I. sumatrana* underwent fermentation in the presence of 540 parts of water, this residue corresponded to 4 per cent. of the original plant. Sample (*b*) consisted of evaporated drainings from the mahl table of the same factory and formed 0·77 per cent. of the original liquid, whereas the origin of sample (*c*) was doubtful.

The samples were neutral, in the main dissolved readily in water, and these liquids on acidification emitted a strong odour of volatile aliphatic acids. When incinerated, all yielded considerable amounts of mineral matter which consisted mainly of the oxides of calcium magnesium and potassium, traces of manganese oxide and alumina being also present.

When agitated with boiling water, a small amount of an insoluble brown precipitate separated which in appearance closely resembled indigo brown, and was found to consist of a mixture of compounds of variable nitrogen content. The main constituent isolated as a dark brown amorphous powder, gave on analysis C = 65·70; H = 5·07; N = 8·03 per cent., figures somewhat lower than those found for the main constituent of indigo brown (*loc. cit.*), whereas the more soluble fraction again contained still more oxygen, C = 64·7; H = 5·0; N = 4·6. From the neutral filtrate a small amount of succinic acid was isolated, the main bulk, approximately 20 per cent. of the "seeth" water residue, consisting of a protein-like compound (N = 8·22) which on heating evolved ammonia and in general property resembled the so-called "indigo gluten" of crude indigo. It consisted of a friable mass, and to the presence of this substance the very hygroscopic nature of the dried "seeth" residue was evidently due.

The following table illustrates the main results obtained by the analysis of the three samples of "seeth" water residue:—

	(a) Per cent.	(b) Per cent.	(c) Per cent.
Nitrogen	2·25	2·77	2·72
Ash	27·30	25·90	26·87
Volatile acids	23·80	21·04	—
Succinic acid	2·21	2·18	—
Brown matter	5·58	12·03	11·18
Indigotin	0·18	0·10	0·082

The Analysis of Indigo.

The methods which have been proposed for the analysis of indigo are of a varied character, and the literature upon the subject is extremely voluminous.

These may be classified as follows: methods (*a*) involving the extraction of impurities with volatile solvents (Schützenberger, Die Farbstoffe, ii., 526); (*b*) the extraction of indigotin with coal-tar oil (Stein, Die Prüfing der Zeugfarben); with aniline (Hönig, Zeitsch. angew. Chem., 1899, 280); with phenol (Brandt, J. Soc. Dyers, 1898, 34); with naphthalene (Schneider, *ibid.*, 1895, 194); with nitrobenzene (Gerland, J. Soc. Chem. Ind., 1897, 108); with acetosulphuric acid (Möhlau and Zimmermann, Zeitsch. farb. text. Chem., 1903, 10, 189); (*c*) the extraction of indigotin by sublimation (Lee, Chem. News, 1884); (*d*) the extraction of indigotin by processes of reduction, lime, and ferrous sulphate (Berzelius), stannous chloride and caustic soda (Dana, Jahres. f. prakt. Chem., 26, 398), zinc and caustic soda (Owen, Amer. Chem. J., 10, 178), grape sugar, alcohol and alkali (Fritzsche, Dingl. poly. J., 1842, 86, 306), and hydrosulphite and lime (Rawson, *loc. cit.*); (*e*) estimation of nitrogen (Voeller, Zeitsch. angew. Chem., 1891, 110).

More important, however, are the methods based upon the titration of a solution of the sulphonated indigo by oxidising agents (*f*) chlorine water (Berzelius), chloride of lime (Chevreul, "Leçons d. chem. appliq. de la teinture," ii.), potassium chlorate and hydrochloric acid (Bolley, Dingl. poly. J., 119, 114), potassium dichromate and hydrochloric acid (J. pr. Chem., 1851, 18, and Schlumberger, Bull. de la Soc. Mullhouse, 1863, 210, 284), potassium dichromate and oxalic acid (Kinley, Chem. News, 1863, 210, 284), potassium ferricyanide (Ullgren, Annalen, 136, 96), and potassium permanganate (Mohr, Dingl. poly. J., 132, 363), and by reducing agents (*g*) sodium hydrosulphite (Müller, Ber., 1880, 13, 2283), and titanous chloride (Knecht, J. Soc. Dyers, 1904, 97, and *ibid.*, 1905, 292).

Finally, (*h*) colorimetric methods (Dingl. poly. J., 27, 54, and 40, 448); (*i*) spectrum analysis (Wollf, Zeitsch. anal. Chem., 17, 65, and *ibid.*, 23, 92); and (*k*) dye trial methods (Chevreul, *loc. cit.*, and Grossmann, J. Soc. Dyers, 1897, 124) have been proposed.

Of these methods of indigo analysis, modifications of Mohr's permanganate process are most generally employed, although others involving the reduction of sulphonated indigo with titanous chloride and sodium hydrosulphite are to some extent in vogue.

The Permanganate Methods.—In order to eliminate the error due to the oxidising action of permanganate upon substances other than indigotin which are present in natural indigo, Rawson, who has been the pioneer in this respect, has devised two processes.

Salting-out Method.—0·5 gram of finely powdered indigo mixed with its own weight of ground glass is sulphonated in a porcelain crucible by means of 20 c.c. of concentrated sulphuric acid at 70° for ½—1 hour; the product is diluted with water to 500 c.c. and the liquid filtered to remove insoluble impurities. 50 c.c. of this solution are mixed with 50 c.c. of water and 32 grams of common salt, and after standing for 1 hour the precipitated sodium indigotin sulphonate is collected and freed from certain soluble impurities by washing with about 50 c.c. of salt solution (sp. gr. 1·2). The precipitate is dissolved in hot water, treated with 1 c.c. of sulphuric acid, diluted to 300 c.c., and titrated with a solution of N/50 potassium permanganate. The liquid gradually takes a greenish tint, and the final disappearance of this constitutes the end point of the reaction. According to Rawson, 1 c.c. of the N/50 permanganate corresponds to 0·0015 of pure indigotin (J. Soc. Dyers, 1885, 74 and 201; "A Manual of Dyeing," Knecht, Rawson and Löwenthal, 1910, 817). Such a factor, however, according to Bloxam (*loc. cit.*) gives too high figures even with pure indigotin, and this has been corroborated by Frank and Lloyd (*ibid.*, 1913, 226) who consider 0·00147 as more correct, and with this Rawson (*ibid.*, 1914, 21) is now in agreement.

Barium Chloride Precipitation Process.—0·5 gram of indigo is sulphonated as before, and after diluting with water, but before making up to 500 c.c., 10 c.c. of a 20 per cent. solution of barium chloride are added. The barium sulphate formed carries down with it the suspended impurities of the indigo, and the clear liquid can be pipetted off and titrated as before. The results are practically identical with those given by the "salting out" method (Rawson, J. Soc. Chem. Ind., 1899, 251).

Bloxam (*ibid.*, 1906, 735) notes that the barium precipitate thus produced is always coloured blue, and this is confirmed by Bergtheil

and Briggs (*ibid.*, 1906, 729). The latter authors contend that the results given by this modification of Rawson are therefore too low, and consider that this defect is obviated by adding instead of barium chloride freshly precipitated barium sulphate to the indigo mixture.

Grossmann (*ibid.*, 1905, 308) throws down the impurities from the indigo solution with calcium carbonate. Bergtheil and Briggs (*loc. cit.*) and also Bloxam (*loc. cit.*) find that some quantity of the colouring matter is also precipitated in this way. Knecht, however, recommends its successful use even in larger quantity (J. Soc. Dyers, 1904, 97, and 1905, 292) in connection with his titanous chloride method; but Bloxam (*loc. cit.*) points out that such being the case this can only be due to the observance of conditions which are not stated in Knecht's paper.

Hydrosulphite Method.—This process, devised by Müller (Ber., 1880, 13, 2283), depends upon the fact that sodium hydrosulphite ($Na_2S_2O_4$) quantitatively reduces pure indigotin sulphonic acids to their corresponding leuco compounds. The solution of the hydrosulphite contained in a stone bottle is covered with a layer of petroleum to prevent oxidation and connected with a supply of hydrogen gas. By means of a siphon, or other convenient arrangement, the liquid can be drawn into a burette. The solution should be equivalent to about 1 c.c.—0·0025 gram of indigotin, and the titrations are performed in an atmosphere of hydrogen or coal gas.

Titanous Chloride Method.—This reagent is much more stable than sodium hydrosulphite, and Knecht (J. Soc. Dyers, 1904, 97, and 1905, 292) was the first to recommend its use for the analysis of indigo. The apparatus employed is similar in character to that required for the hydrosulphite process, and the titration is carried out in an atmosphere of carbon dioxide. If the reduction of the indigotin is effected by the titanium chloride in the presence of mineral acid, no definite end-point can be observed (Knecht), but by the addition of salts of tartaric acid this end-point is rendered quite definite.

In working with natural indigo, Knecht ("Manual of Dyeing"; Knecht, Rawson and Löwenthal, 822) sulphonates 1 gram of indigo with 5 c.c. of 100 per cent. sulphuric acid at 90° for 1 hour. The solution diluted to 300 c.c. is warmed and slowly treated with 12 grams of chalk, cooled, made up to 500 c.c., and 50 c.c. of the clear liquid, to which 25 c.c. of a 20 per cent. solution of Rochelle salt has been added, is titrated whilst boiling with titanium chloride.

On account of the sparing solubility of Rochelle salt, Bloxam (*loc. cit.*) recommends the use of sodium tartrate, but states that the

presence of excess of this or of Rochelle salt (as advocated by Knecht) is to be avoided, or otherwise too high percentages of indigotin are indicated. In the case of pure indigotin (1 gram) sulphonated with 20 c.c. of 100 per cent. sulphuric acid, and made up to 500 c.c. with water, 25 c.c. of this liquid (containing 1 c.c. of acid) requires 4 grams of the sodium tartrate to give quantitative results when titrated with a solution of titanium chloride containing 1 c.c. of concentrated hydrochloric acid per 50 c.c. of solution.

Bloxam (Chem. Soc. Trans., 1905, 87, 975; J. Soc. Chem. Ind., 1906, 25, 735), Orchardson, Wood, and Bloxam (*ibid.*, 1907, 26, 4), and Gaunt, Thomas, and Bloxam (*ibid.*, 1907, 26, 1174) have critically investigated the subject of indigo analysis. Among the methods for preparation of pure indigotin, that involving the crystallisation of crude material from nitrobenzene was discarded as untrustworthy, but the elaborate process of the B.A.S.F. Co. (Brochure, 1900) was found to give a pure substance. On the other hand, sublimation under reduced pressure in Jena flasks immersed in fusible metal at 370—390°, gave, with synthetical indigo of 92 per cent. (approx.) a beautifully crystalline substance, which, after washing with boiling acetic acid, followed by boiling alcohol, was usually chemically pure. The permanganate factor resulting from experiments with these specially purified materials was 1 c.c. of permanganate solution 1/1000 = 0·00222 gram indigotin solution 1/5000, and is in agreement with that previously adopted by the B.A.S.F. Co. Wangerin and Vorlander (Zeitsch. Farben und Textilchemie, 1902, 1, 281) have stated that indigotin suffers loss of strength by oxidation, even when it is sulphonated by 94 per cent. sulphuric acid at 95—100° for half an hour, whereas 8 per cent. fuming acid gives a deterioration of from 2 to 14·2 per cent., according to the time of heating. With the indigotin, however, purified as above, Bloxam showed that heating with 20 per cent. fuming acid for ¾ of an hour at 97° gave no loss, whereas with 30 per cent. acid for 20 minutes at 97°, a deterioration of only 1 per cent. could be observed. In both these cases indigotin tetrasulphonic acid was produced.

The Tetrasulphonate Method.—As a result of these experiments a method for the analysis of indigo based on sulphonation with fuming acid was devised. 1 gram of the indigo, and 2—3 grams of purified sand (powdered glass contains iron, and should not be employed) is treated with 5 c.c. of 25 per cent. fuming sulphuric acid for half an hour in the water oven, and the solution is made up to 500 c.c. with water. 100 c.c. of this solution is treated with 100 c.c.

of potassium acetate solution (450 grams per litre) which causes the precipitation of indigotin tetrasulphonate. The mixture is now warmed, and on cooling finally in ice-water,* the salt completely separates in a crystalline condition. This is collected by means of the pump on a Gooch crucible, and washed free from the brown supernatant liquid with a solution containing 90 grams of potassium acetate and 5 c.c. of acetic acid in 600 c.c. of water. The product is dissolved in 200 c.c. of water, and 20 c.c. of this solution, diluted with 80 c.c. of water, is treated with 0·5 c.c. of sulphuric acid, and titrated with permanganate (1/1000). In order to verify the accuracy of this method, Orchardson, Wood, and Bloxam studied the behaviour of indigo brown and indigo gluten, the main impurities of indigo, when submitted to the analytical process, as this subject had not been investigated by previous workers. Indigo brown when sulphonated with 96 per cent. acid gives, when dissolved in water, a dark-brown liquid, which is attacked by permanganate, though not perhaps so readily as the indigotin sulphonic acids, whereas indigo gluten gives similarly a light yellow solution, which is very rapidly oxidised by the reagent. On the other hand, kaempferol or indigotin yellow, treated in the same manner, gave a product which most readily absorbs permanganate, and, indeed, Rawson (J. Soc. Chem. Ind., 1899, 251) had already pointed out its deleterious effect in indigo analyses. Finally, these authors prepared and submitted to analysis by Bloxam's process mixtures containing known quantities of indigotin and one or other of all of these impurities, with the result that the colouring matter was thus estimated with considerable exactness. Bloxam (Chem. Soc. Trans., 1910, 97, 1473), by an adaptation of the pyridine method for the estimation of indirubin (*loc. cit.*), in which the impurities are eliminated by a process of extraction, has analysed natural indigos, and obtained the same figures as those given by the tetrasulphonate method. Again, by Knecht's titanium chloride method, and employing the modifications above described, this process can also be effectively worked. It is only reasonable to suppose that an analysis based on the selective precipitation of the sulphonated colouring matter is more likely to be efficient than that which presumes the deposition of varied impurities of a diverse chemical character by one specific reagent, and the somewhat lower results given by the tetrasulphonate method, as distinguished from those yielded by the processes previously in use, are in reality due to the

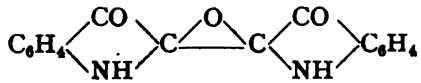
* Prolonged heating should be here avoided, and it is preferable that the solution of the tetrasulphonate with its subsequent recrystallisation should be effected without unnecessary delay.

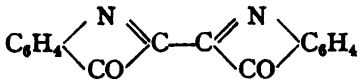
almost complete elimination of these impurities from the indigotin sulphonic acid during the analysis. Rawson (*loc. cit.*) is, however, of opinion that the effect of these impurities on the analytical results has been much overrated; but, on the other hand, no experimental evidence is given in support of this view ("Manual of Dyeing," *loc. cit.*, 818).

The action of potassium permanganate on solutions of the indigotin sulphonic acids is of interest, because the amount of the reagent necessary for the decolorisation of the liquid varies to some extent with the concentration (Rawson, "A Dictionary of Dyes, Mordants," etc., by Rawson, Gardner, and Laycock, 1901, 187). At the concentrations employed by the B.A.S.F. Co., and adopted by Bloxam (*loc. cit.*), 1 gram of indigotin as sulphonic acid requires 0·45 gram of permanganate for decolorisation, whereas the equation

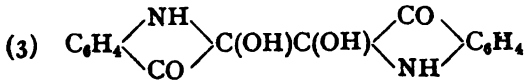
$$5C_{16}H_{10}O_2N_2 + 4KMnO_4 + 6H_2SO_4 = 10C_8H_5O_2N + 2K_2SO_4 + 4MnSO_4 + 6H_2O$$

implies that 0·4824 gram of the reagent is necessary. Again, for the oxidation under similar conditions of indirubin sulphonic acid considerably less permanganate is required, although the oxidation in this case is of a slower character. Bloxam and Perkin (Chem. Soc. Trans., 1910, 97, 1462) consider, therefore, that the oxidation is of a complex nature, and consists either (*a*) of two distinct stages in the formation of isatin sulphonic acid, or (*b*) of two distinct reactions involving the production of two separate substances. According to the first suggestion the isatin sulphonic acid formation would be preceded by that of an intermediate compound (1), whereas by the latter, in addition to isatin sulphonic acid, a dehydroindigotin sulphonic acid (2) may be produced—

(1) 

(2) 

In case the first product of the reaction consists entirely of dehydroindigotin sulphonic acid, this must, prior to further oxidation to isatin sulphonic acid, take up two molecules of water with formation of the sulphonic acid of dihydroxyindigotin (3)—

(3) 

In regard to the very small amount of permanganate required for the decolorisation of the indirubin sulphonic acid a similar explanation can be adopted.

Analysis of Indigos Containing Starch.—It has been shown by Thomson (J. Soc. Dyers, 1911, 27, 49) that the indigotin value of samples of indigo adulterated with starch when estimated by the method of sulphonation and titration with permanganate recommended by Rawson and Bloxam give far too low results. Thus an indigo containing starch by Rawson's method gave 18·8 per cent. of indigotin, whereas after removing the starch with 4 per cent. hydrochloric acid, 35·01 per cent. of indigotin was shown to be present. On the other hand, according to this author when hydrochloric acid is employed in this way for the removal of the starch the analytical results are still too low. Frank and Perkin (J. Soc. Chem. Ind., April, 1912) corroborated these experiments in so far that indigos containing starch give low figures when directly analysed, and it seems evident that a destruction of the indigotin occurs during sulphonation, and is to be attributed to the reducing action of the starch degradation products. As a result, however, of numerous experiments, no loss of indigotin could be observed even by long digestion of mixtures of starch and indigo with boiling dilute hydrochloric acid, and after removal of starch in this manner correct figures were always obtained by the employment of Bloxam's tetrasulphonate process.

Testing of Indigo-dyed Woollen Materials.—An important method for ascertaining the quantity of indigo present on such dyed materials has been devised by Green, Gardner, Lloyd and Frank (J. Soc. Dyers and Cols., 1913, 226; 1914, 15). This consists essentially in removing the indigotin from the fibre with boiling pyridine in a modified form of Soxhlet apparatus, and subsequently concentrating the pyridine solution. The main bulk of the indigotin separates as crystals and to complete the precipitation 50 per cent. of alcohol is then added. The product is collected, washed successively with 50 per cent. alcohol, 2 per cent. caustic soda, hot 1 per cent. hydrochloric acid, hot water, alcohol, alcohol and ether, and finally dried and weighed. It should test 100 per cent. by the tetrasulphonate method.

For fuller details the original paper should be consulted.

The Estimation of Indigos Rich in Indirubin.

It is well known that indirubin is more resistant to oxidation and reduction than indigotin, properties which also apply to the

sulphonic acids of these colouring matters. When dealing, therefore, with sulphonated mixtures of these substances and employing either potassium permanganate, titanium chloride, or sodium hydrosulphite, the indigotin sulphonic acid is to some extent preferentially attacked, so that towards the end of the operation the colouring matter consists entirely of indirubin sulphonic acid. In the case of the first named reagent, however, Koppeschaar (Zeitsch. anal. Chem., 1899, 38, 1) finds that it is not possible to obtain trustworthy analytical figures with indigos in which some quantity of indirubin is present, although Rawson (*loc. cit.*) considers that the indirubin may be approximately estimated in this manner. Bloxam and Perkin (Chem. Soc. Trans., 1910, 97, 1462), however, support the view of Koppeschaar. The latter authors, who also experimented with titanous chloride, show that this reagent behaves in an identical manner towards both indigotin and indirubin sulphonic acids, but although the former is somewhat preferentially attacked, it is not possible in this way to differentiate as to the amount of each of the sulphonated colouring matters which may be present in a mixture of the two. On the other hand, according to Knecht, Rawson, and Löwenthal ("A Manual of Dyeing," 821) indirubin present in mixtures of the two colouring matters may be approximately estimated by the hydrosulphite method.

For analysis of indigos rich in indirubin, processes of extraction based on the greater solubility of the latter have been usually employed.

Extraction with Ether (Rawson, *loc. cit.*).—From 0·1 to 0·25 gram of the sample is boiled with about 150 c.c. of ether for half an hour. When cold the solution is made up to 200 c.c. with ether, mixed with 10 c.c. of water and well shaken. The suspended particles of indigotin settle immediately and a clear solution of indirubin is obtained. A measured quantity of the solution is withdrawn, and compared in a colorimeter with a standard solution of indirubin.

Extraction with Acetic Acid (Koppeschaar, *loc. cit.*).—The indigo is extracted with glacial acetic acid, and the solution, which contains a mixture of indirubin and indigo brown, is treated with caustic soda. The indirubin, which is thus precipitated, is collected, redissolved in acetic acid, and estimated by comparison with a standard solution of the pure colouring matter.

Extraction with Acetone (Gardner and Denton, J. Soc. Dyers, 1901, 170).—0·2 gram of the indigo is digested for half an hour with 100 c.c. of boiling acetone. After cooling the solution is made

up to 100 c.c. with acetone, and then to 200 c.c. with 10 per cent. salt solution, and well shaken. The precipitate of indigotin, indigo brown, and other impurities is removed by filtration, and the indirubin solution estimated colorimetrically with a standard solution of indirubin prepared with acetone and salt solution in a similar way.

Extraction with Pyridine.—Bloxam and Perkin (Chem. Soc. Trans., 1900, 97, 1460) find, as the result of experiments on mixtures of indigotin and indirubin, that neither commercial ether nor acetone are reliable solvents for the complete extraction of indirubin, and that their action, especially in the former case, is chiefly due to the presence of alcohol. Whereas acetic acid is efficient in this respect, and Koppeschaar's process gives approximately good results, pyridine is a much better solvent, and a method for the complete analysis of indigos containing indirubin based on the application of this liquid is described by these authors.

The indigo (0·25—1 gram) evenly incorporated with purified sand (20—30 grams) is introduced into a thin-walled glass tube, termed the "container," closed at one end by means of cotton cloth, on which has been placed a layer of asbestos and purified sand or of sand alone. Sufficient sand is then added to form a layer on the surface of the indigo mixture, which is then covered with asbestos, and the container is now placed in a Soxhlet tube and extracted with boiling pyridine. The extract is distilled down to a small bulk, the residue treated with boiling water and again distilled, and this operation is repeated until the last traces of pyridine have disappeared. The precipitate, which consists of indirubin together with a little indigotin and indigo brown, is collected, freed from the latter by means of dilute alkali, and the residue is sulphonated with 5 c.c. of sulphuric acid at 100°. The product is dissolved in water, filtered, and the amounts of indigotin and indirubin present ascertained by means of the Duboscq tintometer.

The residue in the container is percolated with water, followed with boiling dilute hydrochloric acid to remove indigo gluten, and is now introduced into a beaker and dried. The colouring matter present is sulphonated with 20 c.c. of sulphuric acid in the usual way, the product after dilution is filtered, and the solution of the indigotin sulphonic acid is estimated with permanganate, employing the directions given by Bloxam (*loc. cit.*). Analyses of mixtures of pure indigotin and indirubin, and also of commercial indigos, are given in the paper, and it is also pointed out that by this method an approximate estimation of the indigo brown present in the latter can be carried out.

THE ESTIMATION OF INDICAN IN THE LEAVES OF INDIGO PLANTS.

Although some indication of the indigo-yielding capacity of the plant can be obtained by ordinary steeping experiments, this method was found by Rawson ("Cultivation and Manufacture of Indigo," *loc. cit.*) to possess several drawbacks, and numerous experiments were therefore carried out by him on the quantitative formation of indigo from the leaf extract by the simultaneous action of acids and oxidising agents. As regards the latter, ferric chloride, potassium chlorate, and hydrogen peroxide were tried, but persulphuric acid gave much the best results.

Persulphate Method.—20 grams of leaves are extracted for two minutes with 250 c.c. of boiling water, the solution is strained through muslin, and the residues squeezed and washed with boiling water. The solution is treated with 5 c.c. of 20 per cent. hydrochloric acid, and 40 c.c. of a 5 per cent. solution of ammonium persulphate. The persulphate is not added all at once; at first 2 c.c. are added, after half an hour 2 c.c. more, and again 2 c.c. after another half an hour. After two hours the remainder of the ammonium persulphate is added, and when the mixture has stood for a further period of an hour, the indigo is collected and estimated by permanganate in the usual manner. Bergtheil and Briggs (J. Soc. Chem. Ind., 1906, 734) point out, however, that this process of Rawson's requires modification, as the addition of the reagents at such a high temperature involves a loss of indigotin. The main features of a modification of the process devised by these latter authors are the addition of acid to the cooled extract, and a determination of the course of the reaction, after addition of small amounts of persulphate, by filtration of a portion of the mixture and the addition to the filtrate of a trace of the oxidising agent.

Orchardson, Wood, and Bloxam (*ibid.*, 1907, 40; cf. also Bloxam and Leake, "Research Work on Indigo," Dalsingh, Serai, 1905), who employ sulphuric acid and persulphate, arrived independently at the same conclusion. To 200 c.c. of the leaf extracts these authors add 100 c.c. of a mixture of equal parts of 2 per cent. ammonium persulphate, and 4 per cent. sulphuric acid, and the mixture is kept at 60° for one hour. A comparison of their methods with that of Bergtheil and Briggs indicated an identical result in each case, and an increase of 20—25 per cent. of pure colouring matter in comparison with that yielded by Rawson's original process.

The Isatin Method.—Beyerinck (Proc. K. Akad. Wetensch., 1899, 120), in discussing indican, suggested the possibility that by warm-

ing its solution with isatin and acid a quantitative yield of indirubin might be produced. Orchardson, Wood, and Bloxam (*loc. cit.*) have employed this reaction for the estimation of the leaf, and have devised the following method for this purpose:—

250 c.c. of extract, equivalent to 5 grams of the leaf, is treated with 0·1 gram of isatin, and the mixture boiled for five minutes to expel air, carbon dioxide being passed through the flask. 20 c.c. of hydrochloric acid is then added by means of a tap funnel, and the whole kept boiling for thirty minutes. The precipitate is collected on a tared filter, washed with hot 1 per cent. soda to remove brown compounds, then with 4 per cent. acetic acid and dried. An aliquot portion of the crystalline product is sulphonated, and analysed by the titanous chloride method, adopting the modifications employed by Bloxam (*loc. cit.*). The indirubin thus obtained is usually almost pure (98·5 per cent.), so that for an approximate estimation the latter part of the process is unnecessary. Gaunt, Thomas, and Bloxam (*ibid.*, 1907, 26, 56) have examined the process in greater detail, and point out that by its employment pure indican gives quantitative figures (cf. also Perkin and Bloxam, Chem. Soc. Trans., 1907, 91, 90). On the other hand, this method gives considerably higher figures, both with pure indican (15 per cent.) and the leaf extract (25 per cent.), than those which are obtained by the persulphate process (Orchardson, Wood, and Bloxam; and Gaunt, Thomas, and Bloxam, *loc. cit.*). The unsatisfactory figures in the latter cases arise from a further oxidation of the indigo by the persulphate. That this isatin method does not appear to be affected by other plant constituents was shown by the successful estimation of indican, purposely added to an extract of the leaves of the *Tephrosia purpurea* (Pers.), a plant in which this glucoside is absent.

Efficiency of the Process.

The actual yield of indigotin from the plant during the manufacture is not discussed by Rawson (*loc. cit.*), but this author considers that if the suggestions enumerated in his report are adopted, there is little or no room for a remunerative alteration of the process. Bergtheil, on the other hand, considers that under the conditions he describes (1906, 12) the efficiency is represented by an 82 per cent. yield, or that if to this be added the 5 per cent. believed by Rawson to be retained by the extracted plant, 87 per cent. is thus accounted for. The quantity of indigo estimated refers to the precipitate present in the vat after oxidation, and from this must be, therefore,

deducted the indigo (10—20 per cent.) lost by the "running off" of the "seeth" water, so that the actual yield of dry colouring matter may thus represent from 62—72 per cent. of the theoretical quantity. Recent experiments, however, indicate that by adding aluminoferric to the oxidation a more perfect settlement of the indigo is to be anticipated (*ibid.*, 1909).

Bloxam (Dalsingh Serai Report, and J. Soc. Chem. Ind., 1906, 25, 735), who examined the daily output of indigo (as pressed cake) from the Pembarandah factory, found that the first cuttings of the plant (Moorhun mahai) represented an approximate value of 0·1495 per cent. of indigotin from the plant, whereas the second cuttings gave a value of but 0·1526. Assigning to the plant the low value of 0·3 per cent., a considerable and serious loss is thus apparent. Moreover, the estimation of the results given by the "isatin" method of leaf estimation, and of the finished cake by the "tetrasulphonate" process (*loc. cit.*), both of which have been standardised with extreme care, point to a loss during the manufacture much greater than has hitherto been acknowledged (Report to Government of India, 1908).

Apart from the retention of indoxyl by the residual plant in the steeping vat, and the mechanical carrying over of indigo by the "seeth" water, the deficiency of colouring matter is chiefly to be attributed to the conversion of indoxyl into products other than indigotin. Rawson (*loc. cit.*) has pointed out that if the fermented liquid is allowed to stand before oxidation a considerably decreased yield of indigo is ultimately observed. Thus, on the large scale, by standing for six hours a loss of 16·1 per cent. was apparent. Perkin and Bloxam (*loc. cit.*) have found as a result of their experiments with pure indican, that this alteration or "decay" of indoxyl takes place not only in this manner during the fermentation process, but they consider that the indoxyl from the moment of its production by the hydrolysis of indican until its final conversion into indigotin is continually suffering this alteration. This peculiar reaction is, according to these authors, considerably inhibited by the presence of acid.

Commercial Natural Indigos.

When natural indigo was at its zenith very numerous varieties of this dyestuff were placed on the market, but more recently, owing to its severe competition with the artificial colouring matter, many of these are now rarely met with. From Asia came the indigos of Bengal, Oudh, Madras, Java, Manilla; from Africa those of Egypt

and Senegal; and from America those of Guatemala, Caracas, Mexico, Brazil, South Carolina, and the Antilles.

The best varieties are the Bengal, Java, and Guatemala, although in England the Bengal is now mainly employed. Java indigo, formerly largely esteemed for the manufacture of indigo extract, chiefly because of its general purity, at the present time appears to find its market chiefly in the East.

A good quality of natural indigo has a deep violet-blue colour; it acquires a coppery lustre when rubbed with the finger-nail; it is light, porous, adhering to the tongue, and can be readily broken and ground. Low qualities, which contain much extractive and mineral matter, are dull and greyish in appearance, heavy, tough, and hard, and do not become bronzy by rubbing with the finger-nail.

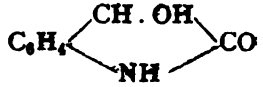
The Properties and Syntheses of Indigotin.

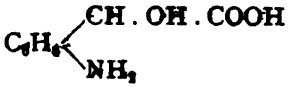
The history of the determination of the constitution of indigotin and of the many syntheses which have been devised for its preparation, leading as they have done to the successful manufacture of the artificial product, constitutes without doubt one of the most interesting chapters in the annals of synthetical organic chemistry. This has been dealt with so fully in other manuals that a brief résumé of the main features of the subject will only be given here, and to avoid detail the main reactions are only expressed by constitutional formulæ.

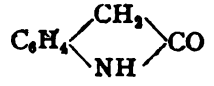
Whereas early work had proved the benzenoid character of indigotin, by the production from it of aniline, anthranilic acid, picric acid and nitrosalicylic acid and isatin, the commencement of a systematic attack on the problem of its structure first dates from the work of Baeyer and Knop (Annalen, 1865, 141, 1).

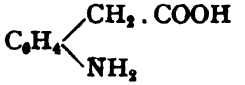
That isatin, $C_8H_5NO_2$, was simply related to indigotin, at that time expressed as C_8H_5NO, appeared probable, and with the hope of reconverting isatin into the latter, its behaviour on reduction was studied by these chemists. The results obtained, though unsuccessful at first in their immediate object, proved to be of considerable importance, and indeed form the basis from which much of our present knowledge of the subject has been derived.

When reduced isatin gives dioxindol (1), oxindol (2), and these substances are now known to respectively consist of the inner anhydrides of *o*-amino-phenylglycollic (3) and *o*-amino-phenylacetic acids (4)—

(1) 

(3) 

(2) 

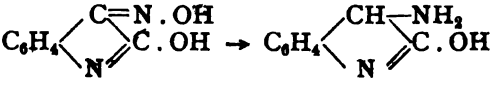
(4) 

By further reduction indole is obtained, and to this, which was subsequently synthesised by Baeyer and Emmerling (Ber., 1869, 2, 680), by fusing *o*-nitro-cinnamic acid with potash and iron filings the formula

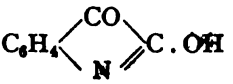
was assigned (Ber., 1870, 3, 517).

The same chemists again by heating isatin with phosphorus oxychloride and acetyl chloride under pressure obtained indigotin.

In 1879 Baeyer and Sinda (Ber., 1878, 11, 584) converted oxindole into isatin according to the following scheme :—



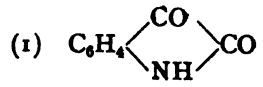
Nitroso-oxindole. Amino-oxindole.

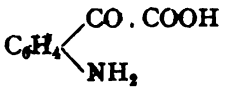


Isatin.

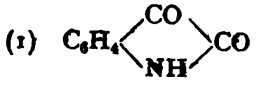
and such a series of reactions formed the coping-stone of the first artificial synthesis of indigotin.

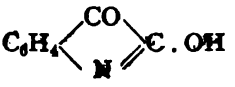
Isatin (1) is the inner anhydride of *o*-amino-phenylglyoxylic acid (isatinic acid) (2)—

(1) 

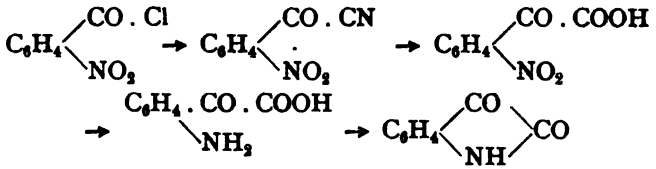
(2) 

and such a constitution was predicted for it by Kekulé in 1869 (Ber., 2, 748). Isatin, which possesses acid properties and is capable of forming metallic compounds, may exist as pointed out by Baeyer in two modifications. These are known as pseudo-isatin (lactam-isatin) (1) and isatin (lactimisatin) (2)—

(1) 

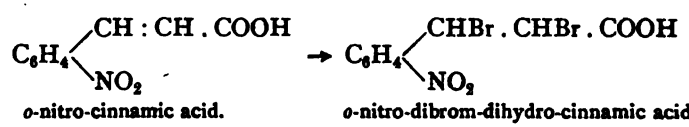
(2) 

A synthesis of isatin from *o*-nitro-benzoyl chloride was announced by Claisen and Shadwell in 1879 (Ber., 12, 350), and the reactions involved may be expressed by the following formulæ :—

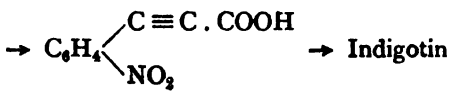


The fact that indole can be prepared from *o*-nitro-cinnamic acid (*loc. cit.*) and that indole is closely related to indigotin, as indeed was shown by Nencki (Ber., 1875, 8, 727), who prepared indigotin by the action of osonised air upon an aqueous suspension of indole, led Baeyer to experiment on the synthesis of indigo from this same acid (Ber., 1880, 13, 254). This object he eventually accomplished by the two methods given below :—

(*a*)

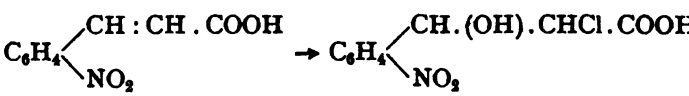


o-nitro-cinnamic acid. *o*-nitro-dibrom-dihydro-cinnamic acid.

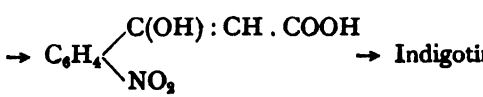


o-nitro-phenylpropiolic acid.

(*b*)



o-nitro-cinnamic acid. *o*-nitro-phenylchlor lactic acid.

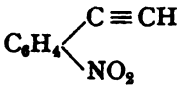


o-nitro-phenylacrylic acid.

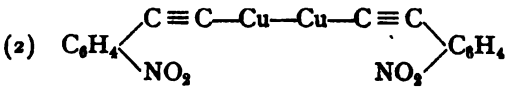
The former method is exceptionally interesting, in that it provided the basis for the first attempt to manufacture indigo on a commercial scale, and though this was hardly successful, the *o*-nitro-phenylpropiolic acid obtained by this method was of some service to the dyeing industry, as a means for obtaining indigo prints on calico.

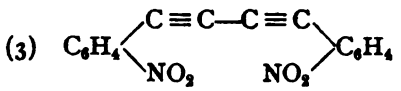
Baeyer, again, in 1882 (Ber., 15, 50) announced a further synthesis employing *o*-nitro-phenylpropiolic acid which was important in con-

nection with the constitution of indigotin. When boiled with water *o*-nitro-phenylpropiolic acid yields *o*-nitro-phenylacetylene—

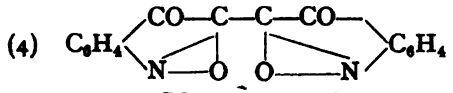


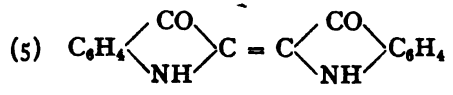
and from the copper compound of this (2) by oxidation with ferricyanide, dinitro-diphenylacetylene (3) is obtained—



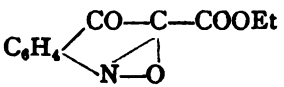


With fuming sulphuric acid this forms diisatogen (4), a compound which on reduction gives indigotin (5)—

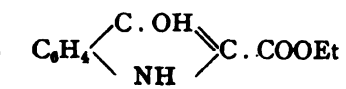


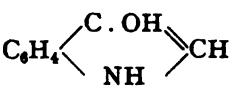


o-Nitro-phenylpropiolic acid, on the other hand, by the action of sulphuric acid (Baeyer, Ber., 1881, 17, 1741) is transformed into its isomer isatogenic acid—



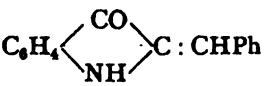
Reducing agents convert this into ethyl indoxylate (1) which by heating gives indoxyl (2)—





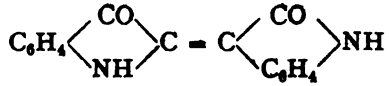
and this latter when oxidised readily passes into indigotin.

Indoxyl reacts with aldehydes and ketones to form the so-called indogenides. Thus with benzaldehyde the indogenide of benzaldehyde (benzylidene pseudo-indoxyl)—



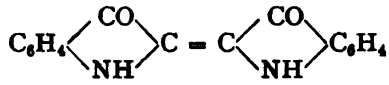
is produced (Baeyer, Ber., 16, 2188).

In a similar way indoxyl condenses with isatin to form indirubin



a colouring matter present in natural indigo (*loc. cit.*), and which is to be regarded as the indogenide of isatin.

Baeyer in 1883 reviewing the facts here enumerated was enabled to deduce the following constitution of indigotin—



which is now accepted as correct. The main arguments he employed in support of this formula are as follows :—

1. Indigotin contains two imido groups.

2. As a result of its formation from diphenylacetylene the carbon atoms of indigotin must be arranged in a similar manner to those present in this substance—

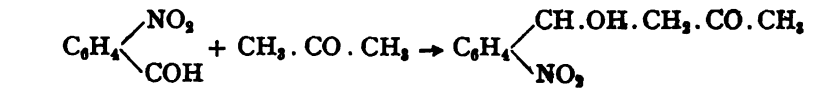
$$C_6H_5 . C . C . C . C . C_6H_5$$

3. Indigotin is only formed from compounds in which the carbon atoms adjacent to the benzene ring are united with oxygen.

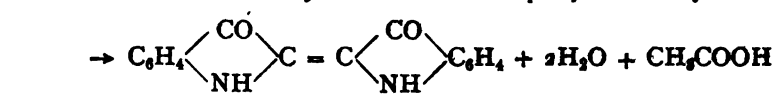
4. The properties of indigotin point to the fact that it is closely related to indirubin.

As a result indigotin is to be regarded as the *a*-indogenide of pseudo-isatin, indirubin itself being the *β*-indogenide. Owing, however, to the lack of activity of the *a*-oxygen atom in isatin, indigotin cannot, like indirubin, be directly prepared from indoxyl and isatin.

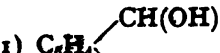
In 1882 (Ber., 15, 2856) Baeyer and Drewsen synthesised indigotin by the action of acetone on *o*-nitro-benzaldehyde in the presence of alkali—



o-nitro-benzaldehyde. *o*-nitro-phenyl-lacto-methyl-ketone.

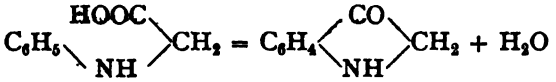


When the acetone is replaced by acetaldehyde *o*-nitro-phenyl-lactic aldehyde (1) is obtained (2), whereas with pyroracemic acid *o*-nitro-cinnamyl-formic acid (2) is produced—

(1)  (2)

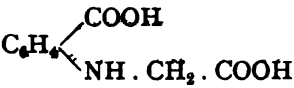
These compounds under the influence of alkali are transformed into indigotin.

Heumann in 1890 (Ber., 23, 2043) devised the synthesis of indigotin from phenylglycocoll (phenylglycine). This on fusion with alkali is transformed into indoxyl which passes readily by oxidation into indigotin—

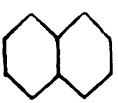


Pseudo-indoxyl.

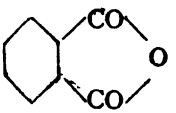
The yield by this method is extremely small, but this can be improved by employing in the place of phenylglycine, phenylglycine *o*-carboxylic acid (Heumann, *ibid.*, 3431)—



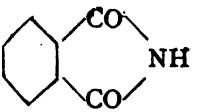
This important reaction forms the basis of the first economical synthesis of indigo, the large scale manufacturing operations of which were perfected by the Badische Anilin und Soda Fabrik in 1897. For the preparation of phenylglycine *o*-carboxylic acid, naphthalene is employed as the starting-point, and the procedure involved will be evident from the following formula:—



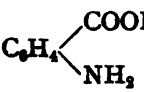
Naphthalene.



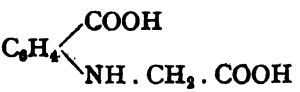
Phthalic anhydride.



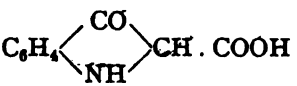
Phthalimide.



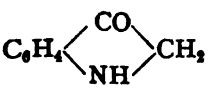
Anthranilic acid.



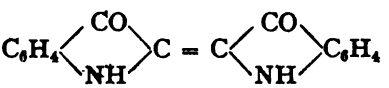
Phenylglycine *o*-carboxylic acid.



Indoxyl carboxylic acid.

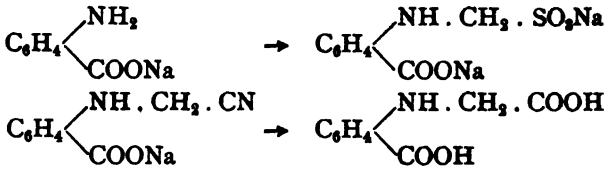


Pseudo-indoxyl.



Indigotin.

An improved method for the production of phenylglycine *o*-carboxylic acid from anthranilic acid has subsequently been adopted, the reagents employed being formaldehyde, bisulphite, and potassium cyanide—



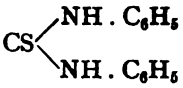
Phenylglycine can be prepared directly from aniline by the same method—

$$C_6H_5NH_2 + CH_2O + HCN \rightarrow C_6H_5NH_2CH_2CN$$
$$\rightarrow C_6H_5NH \cdot CH_2COOH$$

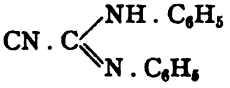
More recently it has been recognised that the unsatisfactory yield of indigo by the original process of Heumann is due to the presence of water in the alkali fusion. By the replacement of the sodium hydroxide with sodium amide the destructive action of the water is avoided and the fusion can be successfully carried out at a lower temperature. The manufacture of indigo by such a method has been more recently adopted by the firm of Meister Lucius & Brüning at Höchst.

Interesting is also the fact that by treatment with fuming sulphuric acid phenylglycine is converted into indigotin disulphonic acid.

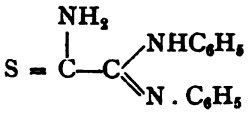
Of other indigo syntheses that of Sandmeyer, at one time employed on the manufacturing scale, is of importance. The starting-point in this method is thio-carbanilide—



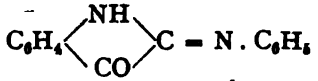
obtained by the action of carbon disulphide on aniline. This compound by the action of potassium cyanide and lead carbonate forms hydrocyano-carbodiphenylimide—



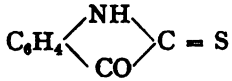
which on treatment with ammonium sulphide gives the thio-amide—



The latter by heating with sulphuric acid is converted into isatin anilide—



and from this by reduction with sulphuretted hydrogen in acid solution thio-isatin is obtained—



By the action of dilute alkalis thio-isatin readily passes into indigotin.

LONCHOCARPUS (*Lonchocarpus cyanescens*).

The *Lonchocarpus cyanescens* (Benth.), a leguminous plant of the sub-order *Paplionaceae*, is a woody-climber from 10 to 14 feet long. The young leaves contain an indigo-yielding principle, and on this account the plant is employed by the tribes of Sierra Leone and the interior and those of Western Soudan as the source of a blue dye. In the former country the young leaves are collected along with some more matured ones, roughly pounded, and dried in the sun. In this state it is sent into the market as "Gara," and sold to the dyers. The natives of Western Soudan employ the young and tender buds, which are collected, pounded when quite raw, made into balls, and dried in the sun. For dyeing purposes the "Gara" is covered with water, treated with potash and the bark of the *Morinda citrifolia* (Linn.) and allowed to ferment for some days. The cloth to be dyed is thrown into the vat, left there for some time, and dried in the sun. An examination of "Gara" by Perkin indicated the presence of approximately 0·62 per cent. of indigotin (J. Soc. Chem. Ind., 1907, 389). Apparently also this plant is utilised in Northern Nigeria as a dyestuff in the form of a similar preparation to that described above, and for the manufacture of a crude indigo. A sample of this Nigerian leaf product contained approximately 0·65 per cent. of indigotin, whereas in the indigo the presence of 21·47 per cent. of indigotin and 1·33 per cent. of indirubin was detected (Perkin, J. Soc. Chem. Ind., 1909, 353). The botanical examination of the former, and also of plant débris contained in the latter, by V. H. Blackman, indicated that they were derived from the *L. cyanescens*, or some closely related form. Rawson and Knecht (J. Soc. Dyers, 1888, 66) have described similar leaf and crude indigo products, which had been sent to this country by Sir T. Goldie, Governor of

the Royal Niger Co., and these respectively contained 0·51 per cent. of indigotin and 39·12 per cent. of indigotin, together with 4·75 per cent. of indirubin. A more recent examination of the leaf fragments in Rawson and Knecht's samples has shown that these possess the same structure as those of the *L. cyanescens* (Perkin, *loc. cit.*), and it thus appears evident that in Western Africa this plant is extensively employed for dyeing and the preparation of indigo. There is reason to presume that the indigo yielding principle present in the young leaves of the *L. cyanescens* gradually disappears when these reach maturity, as samples of the latter examined in this country were devoid of indigo-producing property. The *L. cyanescens* is probably identical with the "Taroom akkar" described by Bancroft ("Philosophy of Permanent Colours," 1813, i., 189 and 191).

Woad (*Vouède*, *Pastel*, Fr.; *Waid*, Ger.).

This commercial product is a dark clay-like preparation made from the leaves of the woad-plant, *Isatis tinctoria* (Linn.), an erect, herbaceous, biennial plant, belonging to the *Cruciferæ*, bearing yellow flowers, small flat elliptical pods, and large smooth lanceolate or spathulate leaves.

The term "woad" is derived from the Saxon "wad," which it has been suggested is derived from Woden, the Saxon God of War. It is synonymous with the Gallic *glastum*, with which, according to Pliny, the ancient Britons dyed their skin blue, in time of war and in connection with certain religious observances.

The plant is a native of Southern Europe, and from very early times has been employed in dyeing blue, for which purpose, previous to the introduction of indigo from India, it was largely cultivated in various parts of Europe—e.g. Thuringia, Languedoc, Piedmont, etc. Its cultivation has now declined almost to the vanishing-point.

In this country woad is now only grown, to a very small extent, in the fen lands of Lincolnshire and Huntingdon. The seed is sown in the early spring, March or April, and the young plants having been duly thinned and weeded, the leaves are ready for the first plucking in June, which, at intervals of five or six weeks, is repeated once or twice, or as often as fresh leaves shoot up.

The newly-gathered leaves are at once crushed or ground in edge-runner mills to a pulp, which is then placed in small heaps to drain, till sufficiently dry to cohere and be submitted to the "balling" process. This consists in working the pasty mass by hand into balls, 4—6 ins. in diameter. These are at once spread out on wicker-work trays or "fleaks," and thoroughly dried in well-ventilated

sheds. The balls are stored in a dry airy place till the whole crop has been gathered, and are then submitted to the so-called "couching"—i.e. a fermentation—process. For this purpose the balls are ground to a coarse powder, which is spread on the floor of the couching-house to a depth of 2 or 3 feet, and there reduced again to the consistency of a paste by frequent sprinkling with water and turning over with shovels. During this process, which lasts from twenty to forty days, the mass becomes heated and abundant offensive odours are given off. The operation needs to be conducted with some care and skill, so that the fermentation is neither so slow that a "heavy" product is obtained, nor so rapid as to give one which is "foxy". When the fermentation has subsided, and the stiff, pasty mass is sufficiently cooled, it is packed in casks ready for the market.

It has been calculated that 9 parts by weight of woad leaves yield 1 part of the prepared product.

Although woad was formerly used for the indigo contained in it, it is at present only employed for the purpose of exciting fermentation in the indigo-vat ordinarily used by the woollen dyer, which is therefore termed the "woad-vat".

According to Wendelstadt and Binz (Ber., 1906, 39, 1627) woad contains two distinct micro-organisms, one of which under suitable conditions appears to be able to reduce indigo.

Spurious woad was sometimes prepared from the leaves of the rhubarb, cabbage, etc., but these products were very inferior to the true woad.

The colouring principle of woad leaves, considered by Schunck to be identical with that present in the *Indigoferæ*, is now known to be a distinct substance. This has not been isolated in a pure condition, but in its general reactions resembles indoxylic acid (see INDIGO, NATURAL).

Other Literature.—Chevreul, J. Pharm. Chim., 1808, 66, 369; 1817, 350; Ann. Chim. Phys., 68, 284; Gilbert, Annalen, 41, 245; 42, 315; Trommsdorff, J. Pharm. Chim., 19, 93; Paris, Mus. Hist. Nat. Ann., 18, 251.

PURPLE OF THE ANCIENTS.

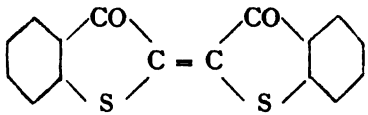
The ancients derived their purple from certain molluscs or sea-snails, the *Purpura hoemastoma*, known to Pliny as *Buccinum*, and from the *Murex brandaris*, called by Pliny *Purpura*. At Athens and Pompeii, large quantities of the shells have been discovered lying in heaps close to ancient dyeworks. These molluscs are to be

ound throughout the whole of the Mediterranean, and indeed, in the sea in numerous parts of the world varieties exist which may be employed for dyeing purposes. Two sorts of purple, known as Tyrian and Byzantium purple, were recognised by the ancients, the former possessing a redder tint than the latter.

From the observations of Cole (Phil. Trans., 1685), Réaumur (Mem. de l'Acad. Royale des Sciences, 1711) and Bancroft ("Philosophy of Permanent Colours," 1, 120, 1813), it appears that the colour-producing secretion, which resembles pus in appearance and consistence, is contained in a small whitish cyst or vein, placed transversely under, but in immediate contact with the shell, and near the head of the animal. This pus-like matter, either diluted with water or undiluted, on being applied to bits of white linen or calico, and exposed to sunlight, rapidly changes its colour, passing from yellow, through light green, deep green, and "watchet blue," to purplish-red or crimson. To produce this change of colour the light of the sun is essential. It is effected more rapidly by the direct action of the sun's rays than by that of diffused light, but it does not take place in moonlight or in artificial light. If the linen or other fabric to which the secretion has been applied is kept in the dark, it remains unchanged, but when exposed to the sun it becomes purple, even after the lapse of years, though a little more slowly than at first. The metamorphosis which the change of colour indicates is not sensibly promoted by heat. It proceeds in a vacuum and in hydrogen or nitrogen gas as speedily as in air on exposure to light. The colour produced is remarkably stable, resisting the action of soap, alkalis, and most acids, being destroyed only by nitric acid and chlorine (see also Bizis, Journ. de Ch. Med., 1835, 10, 99, and A. and G. de Negri, Gazz. chim. ital., 1875, 437). Schunck (Chem. Soc. Trans., 1879, 35, 591) who examined the *Purpura capillus*, which he procured from the rocks at Hastings, finds that the colouring matter (punicin) is quite insoluble in water, alcohol, or ether, sparingly soluble in boiling benzene or boiling glacial acetic acid, and readily soluble in boiling aniline, giving a solution which is at first green, but as it approaches saturation becomes purplish-blue. At this point it shows a broad, well-defined absorption band, beginning near C and extending beyond D; but as the solution cools, depositing the substance contained in it, the colour changes to green, and the band becomes gradually narrower, until it occupies the space midway between C and D, and then disappears. The colouring matter as deposited from the solution in aniline is seen, under the microscope, to consist of star-shaped groups of irregular crys-

talline needles, which, when very thin, show by transmitted light a purple colour. Punicin is soluble in oil of vitriol, giving a dirty purple colour, and showing a broad ill-defined absorption-band between D and E, the green and blue of the spectrum being much darkened. On heating the solution slightly, or allowing it to stand for some time, the colour changes to a bright bluish-green and it now shows an absorption-band in the red. Punicin is also sparingly dissolved by a hot alkaline solution of stannous oxide, and the solution on exposure to air becomes covered with a blue pellicle. Punicin may be sublimed, giving crystals which show by reflected light a semi-metallic lustre, like that of sublimed indigo-blue (Schunck, *loc. cit.*). Witt (Technologie der Gespinnstfasern, 1888) expressed the opinion that the colouring matter yielded by these molluscs was an admixture of indigotin with a red colouring matter not so fast to light.

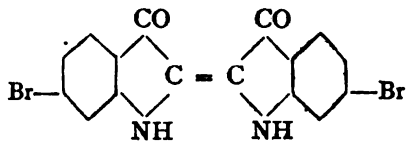
Friedländer (Annalen, 351, 390; Ber., 1906, 39, 1060) has examined the dye yielded by the *Murex brandaris* and *Murex trunculus* which he obtained from the zoological station at Trieste. Letellier (Comptes rend., 1891, 109, 82) had observed that, in addition to the colouring principle, organic sulphur compounds were also present in these glands, and it suggested itself, therefore, to Friedländer as possible that the "purple of the ancients" might in reality consist of the thioindigotin—



which he had lately discovered.

To isolate the colouring matter the glands of the molluscs were spread out as thinly as possible upon filter paper, which was then exposed to the sunlight for half an hour. The highly coloured product was now immersed in diluted hydrochloric acid (1 : 1), the mixture evaporated to dryness on the water-bath, the residue extracted with hot water, and washed with alcohol and ether. In this manner a product consisting only of cellulose and the pure colouring matter was obtained, and the latter could be readily removed by extraction with boiling anisole, from which it separates in the crystalline condition. Finally, it was recrystallised from nitrobenzene. It consists of dark violet crystals which possess a coppery lustre, dissolves in hot, high-boiling solvents with a blue-violet colour, yields a sublimate on heating, and in numerous respects resembles the colouring matters of the indigo group. Analysis indicated the absence of

sulphur, although nitrogen was found to be present. The absorption spectrum is similar to that given by indigotin; but, on the other hand, it is distinguished from this latter colouring matter by its sparing solubility, and by giving with cold concentrated sulphuric acid a reddish-violet coloration. With fuming sulphuric acid it yields a soluble blue sulphonic acid, and when reduced in alkaline solution forms a pale yellow liquid, from which, when exposed to air, it separates as a reddish-violet precipitate. In a later paper by the same author (Ber., 1909, 42, 765) some slight modifications of the method for the isolation of the dye from the *Murex brandaris* are given, and it is shown that in this manner about 12,000 molluscs are required for the preparation of 1·4 grams of the substance. This colouring matter contains bromine, and by a comparison with the synthetic dye, there can be no doubt that it is in reality 6 : 6′ *dibromo-indigotin*—



Further investigation has indicated that in addition to this dibrom-indigotin another dye of a bluer shade, also containing bromine, but possessing a greater solubility in organic solvents, is produced from the *Murex brandaris*. It contains more carbon and less bromine than dibromindigotin, but its constitution is as yet undetermined (Friedländer, Chem. Zeit., 1911, 640).

CHAPTER XVI.

LICHENS, LICHEN ACIDS, AND COLOURING MATTERS DERIVED THEREFROM.

Lichens—Orsellinic Acid—Lecanoric Acid—Evernic Acid and Everninic Acid—Ramalic Acid—Erythrin—Atranorin—Barbatic Acid—Orchil and Cudbear—Litmus.

LICHENS.

MANY species of lichens have been employed from the earliest times in medicine, dyeing, and as foodstuffs ("Mémoires sur l'utilité des lichens," par Hoffmann, Amoreux et Willemet, Lyon, 1787). From about the year 1300, certain species have been utilised for the production of the purple dyestuff "archil" or "orchil," since, as shown by modern researches, they contain colourless principles, derivatives of orcin, which under the influence of ammonia and atmospheric oxygen yield the purple colouring matter known as orcein (*v.* ARCHIL). Under the name of *Crottle* or *Crotal*, with various descriptive prefixes, several species have been, and still are to a very limited extent, directly applied in dyeing buff and brown colours on homespun yarn in the Highlands of Scotland, Wales, etc. Those lichens, e.g. Iceland moss (*Cetraria islandica*, Ach.), which serve as foodstuffs, contain a starch-like substance termed *lichenin*, which is capable of conversion into glucose.

Our earlier chemical knowledge of the constituents of many of these lichens is mainly due to the work of Knop, Rochleder, Heldt, Schunck, Schmidt, Stenhouse, Stenhouse and Groves, and Weppen, whereas for the later very numerous investigations we are chiefly indebted to the chemists Oswald Hesse and Wilhelm Zopf. As a result, a very large number of new compounds have been isolated and described, the constitutions of which in most cases, however, are as yet undecided. On the other hand, considerable advance has been made as regards the exact structure of some of the more common constituents, viz. atranorin (atranoric acid), barbatic acid, evernic acid, erythrin (erythric acid), lecanoric acid, and ramalic acid, and the chemistry of these substances is dealt with under their special headings.

As the work of Hesse (H.) is mainly to be found in the Journal für praktische Chemie, and that of Zopf (Z.) in the Annalen, to avoid frequent repetition the year only of the papers published in the journals is noted below.

Trachylia tigillaris, Fr. (*Acolium tigillare*; *Calicium tigillare*, *Cyphelium tigillare*), rhizocarpic acid, $C_{28}H_{20}O_7$ (H.), melting-point 177—178°, and acolic acid (H. 1900).

Acarospora chlorophana, rhizocarpic acid, pleosidic acid, $C_{17}H_{28}O_4$, melting-point 131—132° (Z. 1903).

Alectoria implexa, Nyl. (*A. cana*), zeorin, salazinic acid (Z. 1898). *A. ochroleuca*, usnic acid, $C_{18}H_{16}O_7$, and barbatic acid (Z. 1899). *A. sarmentosa*, usnic acid (Z. 1900). *A. jubata*, var. *implexa*, salazinic acid, alectoric acid, $C_{28}H_{24}O_{15}$, melting-point 186°. *A. articulata*, *d*-usnic acid, usnaric acid, $C_{30}H_{22}O_{16}$, melting-point 240—260°. *A. canariensis*, *d*-usnic acid, usnaric acid (H. 1902). *A. implexa*, atranorin (H. 1906).

Anaptychia ciliaris, atranoric acid (atranorin). *A. speciosa*, atranorin, zeorin, $C_{52}H_{88}O_4$ (Z. 1895—1897).

Aspicilia calcarea, erythric acid, oxalic acid, aspicilin, melting-point 178·5° (H. 1900). *A. gibbosa*, aspicilic acid, melting-point 150° (H. 1904).

Baeomyces roseus, an acid, melting-point 180° (H. 1898).

Biatora lucida, rhizocarpic acid, $C_{28}H_{20}O_7$, atranorin (Z. 1897; H. 1907); no usnic acid (cf. Knop, 1843). *B. mollis*, diffusic acid (Z. 1905). *B. Lightfootii*, *l*-usnic acid (Z. 1906). *B. grandulosa*, gyrophoric acid, $C_{16}H_{14}O_7$ (Z. 1906).

Blastenia arenaria (*Callopisma erythrocarpa*), phytosterol, blasterin, melting-point 170° (H. 1898). *B. arenaria*, atranorin, gyrophoric acid, $C_{16}H_{14}O_7$ (H. 1898). *B. Jungermanniæ*, parietin (Z. 1906).

Calycium crysocephalum, vulpic acid (H. 1898; Z. 1895). *C. chlorinum* or *chlorellum*, vulpic acid (Z. 1895); pulvic acid and traces of leprarin, $C_{19}H_8O_9$ (Kassner, Arch. Pharm., 239, 44; H. 1900). *C. flavum*, chrysocetraric acid, $C_{19}H_{14}O_8$ (H. 1900). *C. Stenhammari*, calycin, $C_{18}H_{12}O_5$ (Z. 1895).

Callopisma flavovirescens, chrysophanic acid, physcion, $C_{16}H_{12}O_5$ (H. 1902). *C. vitellinum*, calycin (Z. 1895); callopismic acid and mannitol (Z. 1897).

Rhizocarpon oreites, A. Zahlbr. (*Catocarpus oreites*), rhizocarpic acid, $C_{28}H_{20}O_7$, psoromic (parellic) acid, $C_{21}H_{16}O_9$ (Z. 1905).

Cetraria cucullata (*Platysma cucullatum*), protolichesteric acid, $C_{18}H_{32}O_5$ (Z. 1902). *C. chlorphylla*, protolichesteric acid and

atranorin (Z. 1902). *C. complicata*, protocetraric acid, $C_{30}H_{22}O_{15}$, *l*-usnic acid, and atranorin.

Cetraria islandica contains starch not deposited in granules, but uniformly distributed among the cells (lichenin). The lichenin, which is convertible into sugar, is present in such large quantity that this lichen can be used for food (Schmidt, Annalen, 51, 29). There is also said to be present cetraric acid, lichenstearic acid (Knop and Schaedermann, Annalen, 55, 114), protocetraric acid, and proto-*a*-lichesteric acid (Z. 1902; H. 1903 and 1904), α-lichenostearic acid, $C_{18}H_{30}O_5$ (melting-point 122—123°), β-lichenostearic acid, $C_{18}H_{30}O_5$ (melting-point 121°), γ-lichenostearic acid, $C_{18}H_{30}O_5$ or $C_{19}H_{32}O_5$ (melting-point 121—122°), paralichenostearic acid, $C_{20}H_{34}O_5$, dilichenostearic acid, $C_{36}H_{60}O_{10}$, and cetraric acid, $C_{26}H_{20}O_{12}$ (H. 1898).

C. nivalis, usnic acid (Z. 1904). *C. stuppea*, protolichesteric acid (Z. 1904). *C. aculeata* or *Cornicularia aculeata*, protolichesteric acid (Z. 1904); lichenin and lichenic (fumaric) acid. *C. pinastri*, pinastric acid, $C_{16}H_8O_8$ (Z. 1895). *C. glauca* (*Platysma glaucum*), lichenin (Berzelius). *C. juniperina*, chrysocetraric acid, $C_{19}H_{14}O_6$, usnic and vulpic acids (H. 1898). *C. pinastri*, chrysocetraric, usnic and vulpic acids (H. 1898; Z. 1899). *C. fahlunensis*, cetraric acid (Z. 1898).

Candelaria concolor, callopismic acid or ethyl-pulvic acid, $C_{20}H_{16}O_5$, dipulvic acid, $C_{32}H_{22}O_9$ (Z.); calycin, and stictaurin, $C_{18}H_{12}O_5$ (H.; Z. 1899). According to Hesse, 1898, dipulvic acid is a mixture of calycin and pulvic anhydride. *C. vitellina*, stictaurin (Z. 1899), calycin and pulvic anhydride (Z. 1899).

Cladina silvatica, usnic acid and cetraric acid (Z. 1898). *C. alpestris*, usnic acid (Z. 1898). *C. rangiferina*, cetraric acid and atranorin (Z. 1898) and usnic acid (H. 1898). *C. pyxidata*, parellic acid (H. 1898). *C. coccifera*, cocellic acid, $C_{20}H_{22}O_7$ (H. 1898). *C. uncialis*, *d*-usnic and thamnolic acids, $C_{20}H_{16}O_{11}$ (Z. 1902).

Cladonia amaurocraea, usnic acid (Z. 1898). *C. alcicornis*, usnic acid (H. 1902). *C. deformis*, usnic acid (Z. 1900). *C. cyanipes* usnic acid (Z. 1900). *C. Floerkeana*, cocellic and thamnolic acids (H. 1900). *C. rangiformis*, atranorin, rangiformic acid

$$C_{20}H_{23}O_5 \cdot OMe$$

(H. 1898). *C. uncinata* (no usnic acid, see Knop, Annalen, 1844, 49, 120); but uncinatic acid, $C_{23}H_{28}O_9$ (H. 1900). *C. destricta* (*C. uncialis*), usnic acid and starch (Knop, *ibid.*, 119); *l*-usnic acid (Salkowski, Annalen, 1901, 319, 391). *C. incrassata*,

l-usnic acid (S.). *C. glauca*, squamatic acid (Z. 1902). *C. strepsilis*, thamnolic acid and strepsilin (Z. 1903). *C. thamnolis*, thamnolic acid, $C_{20}H_{18}O_{11}$, and strepsilin. *C. destricta*, *l*-usnic acid (Z. 1903); *l*-usnic and squamatic acids and cladestin (H. 1904). *C. macilenta*, usnic acid and starch (Knop, *loc. cit.*); rhizonic acid (Z. 1903). *C. squamosa*, var. *ventricosa*, squamatic acid (Z. 1904). *C. squamosa*, var. *denticollis*, squamatic acid (Z. 1907). *C. fimbriata*, var. *simplex*, fumaroprotocetraric acid and fimbriatic acid (Z. 1907). *C. fimbriata*, var. *cornuto-radiata*, fumaroprotocetraric acid (Z. 1907). *C. pityrea*, var. *cladomorpha*, fumaroprotocetraric acid (Z. 1907). *C. silvatica*, var. *condensata*, *l*-usnic acid (Z. 1907). *C. verticillata*, var. *subcervicornis*, fumaroprotocetraric acid (Z. 1907), atranorin and cervicornin. *C. chlorophæa*, fumaroprotocetraric acid. *C. gracilis*, var. *chordalis*, fumaroprotocetraric acid (Z. 1907). *C. crispata*, var. *gracilescens*, squamatic acid (Z. 1907). *C. coccifera*, cocellic acid, $C_{20}H_{22}O_7$ (H. 1895). *C. incrassata*, *l*-usnic acid (Z. 1905). *C. rangiferina* usnic acid (Rochleder and Heldt, Annalen, 48, 2); lichenin (Schmidt, *ibid.*, 51, 29); cladonic acid (*β*-usnic acid), $C_{18}H_{16}O_7$ (Stenhouse, *ibid.*, 155, 58); *d*-usnic acid (no *l*-usnic) and silvatic acid,

$$CO_2Me \cdot C_{18}H_{24}O_3 \cdot COOH$$

(H. 1907); atranorin and fumaroprotocetraric acid (Z. 1906). *C. rangiferina*, var. *vulgaris*, atranorin and protocetraric acid (H. 1898). *C. rangiferina*, var. *silvatica*, *d*-usnic acid (Z. 1906); usnic and protocetraric acids (H. 1898). *C. pyxidata*, lichenin (Schmidt, Annalen, 51, 29); emulsin (Hérissey, J. Pharm. Chim., 1898, [vi.], 7, 577).

Cornicularia aculeata, rangiformic acid (H. 1902).

Chiodecton sanguineum (*C. rubrocinctum*), chiodectonic acid,

$$C_{14}H_{18}O_5$$

Cyphelium trichiale, var. *candelare*, calycin (Z. 1906).

Darbishirella gracillima, parellic acid (H. 1898).

Dendographa leucophæa, protocetraric acid (H. 1898); erythrin and orcinol (Ronceray, Bull. Soc. chim., 1904, [iii.], 31, 1097).

Dimelaena oreina, zeorin and usnic acid (Z. 1897).

Diploicia canescens (*Catolechia canescens*), diploicin, melting-point 225°, catolechin, melting-point 214—215°, and atranorin (Z. 1904).

Diploschistes scruposa, diploschistessic acid, $C_{15}H_{16}O_7$ (Z. 1906).

Endorcarpon miniatum (*a*) *vulgare*, phytosterol and an acid (H. 1898).

Evernia divaricata, divaricatic acid, $C_{21}H_{22}O_6 \cdot OMe$ (H. 1900), and usnic acid (Z. 1897); no usnic acid (H.). *E. furfuracea*, usnic

acid (Rochleder and Heldt, Annalen, 48, 9); no usnic acid, but erythric acid (Z. 1897), or rather olivetoric acid, $C_{27}H_{36}O_8$ (Z. 1900) physodic acid, physodylic acid, $C_{23}H_{26}O_9$, and furevernic acid (H. 1907); atranorin, evernuric acid, $C_{22}H_{24}O_8$, and furevernic acid, but no erythric or olivetoric acids (H. 1906); emulsin (Hérissey, J. Pharm. Chim., 1898, [v.], 7577). *E. prunastri*, evernic acid, atranorin (Z. 1897); evernic acid, usnic acid and atranorin and chrysocetraric acid (H. Annalen, 1895), $C_{19}H_{14}O_6$. *E. thamnodes*, divaricatic acid, usnic acid (Z. 1897; H. 1900). *E. vulpina*, vulpic acid and atranorin (H.). *E. illyrica* (Dalmatia), divaricatic acid and atranorin (Z. 1904). *E. ochroleuca*, usnic acid (Knop, Annalen, 49, 122).

Everniopsis Trulla, salazinic acid and atranorin (Z. 1897).

Gasparrinia medians (*Physcia medians*) calycin, rhizocarpic acid (H. 1898); pulvic lactone (H. 1903). *G. sympagea*, parietin (Z. 1905). *G. elegans* (*Physcia elegans*), physcion (H. 1898). *G. murorum*, physcion (H. 1898). *G. decipiens*, physcion (H. 1898). *G. cirrhochroa*, chrysophanic acid (Z. 1897).

Graphis scripta, salazinic acid (H. 1900).

Gyalolechia aurella, calycin (Z. 1895), callopismic acid (Z. 1897), stictaurin (Z. 1899).

Umbilicaria pustulata (Hoffm.). (*Gyrophora pustulata*), gyrophoric acid, $C_{36}H_{36}O_{15}$ (Stenhouse, Annalen, 70, 218), $C_{16}H_{14}O_7$ (H.). *G. hirsuta*, gyrophoric acid (Z. 1898). *G. deusta*, gyrophoric acid (Z. 1898). *G. polyphylla*, umbilicaric acid, $C_{25}H_{22}O_{10}$ (Z. 1898); umbilicaric acid and gyrophoric acid (H. 1898, 1901). *G. hyperborea*, umbilicaric acid (Z. 1898). *G. deusta*, umbilicaric acid (Z. 1898). *G. vellea*, gyrophoric acid and gyrophorin, melting-point 189° (Z. 1899). *G. spodochroa*, var. *depressa*, gyrophoric acid (Z. 1900). *G. polyrrhiza*, umbilicaric acid, lecanoric acid, gyrophoric acid (Z. 1905).

Hæmatomma ventosum, divaricatic acid, $C_{22}H_{26}O_7$, melting-point 149° (Z. 1898); *d*-usnic acid, divaricatic acid, and an acid resembling alectoric acid (H. 1900). *H. coccineum*, var. *leiphæmum*, leiphaemin, melting-point 193°, atranorin, zeorin (Z. 1902). *H. coccineum*, var. *abortivum*, coccic acid, $C_{12}H_{16}O_{10}$, $3H_2O$, melting-point 262—264°, atranorin, haematomin, $C_{10}H_{10}O$ or $C_{20}H_{32}O_2$, melting-point 143—144°, and haematommidin, melting-point 194—196° (Z. 1903); no zeorin (H. 1907). *H. coccineum*, var. (?) lecanoric acid, (H. 1907). *H. coccineum*, var. (?) (from Wildbad), coccic acid, atranorin, zeorin, hydrohaematommin, $C_{10}H_{18}O$, melting-point 101° (H. 1906). *H. coccineum*, *l*-usnic acid, zeorin, atranorin, porphyrillic

acid, hymenorhodin, and leiphaemin (Z. 1906). *H. leiphæmum*, atranorin, zeorin, leiphaemin, leiphaemic acid, $C_{22}H_{46}O_5$, melting-point 114—115° (Z. 1903). *H. porphyrium*, atranorin, zeorin, porphyrilic acid, leiphaemin, hymenorhodin (Z. 1906).

Pertusaria dealbata, Nyl. f. *corallina*, Cromb. (*Isidium corallinum*) ("white crottle"), calcium oxalate (Braconnot, Ann. Chim. Phys., [ii.], 28, 319).

Lecanora atra, atranoric acid (atranorin), $C_{19}H_{18}O_8$, and a yellow crystalline substance (Paternó and Oghaloro, Gazz. chim. ital., 1877, 7). Hesse (Ber., 10, 1324) considers the atranoric acid to be hydrocarbonusnic acid, and the yellow substance to be cladonic acid. Obtained from certain districts it contains lecanorol (Z. 1897), $C_{27}H_{30}O_9$, H_2O. *L. varia*, psoromic acid and *l*-usnic acid (Z. 1905). *L. grumosa*, atranorin and lecanorol (Z. 1897). *L. cenisea*, atranorin and roccellic acid, $C_{17}H_{32}O_4$ (cf. Schunck and Hesse, *Roccella tinctoria*). *L. sordida*, atranorin, zeoric acid (Z. 1897). *L. sordida*, var. *glaucoma*, atranorin and parellic acid (H. 1898). *L. sordida*, var. *Swartzii*, atranorin, thiophanic acid, $C_{12}H_6O_{12}.H_2O$, melting-point 242°, roccellic acid, lecasteric acid, $C_{10}H_{20}O_4$, melting-point 116°, and lecasteride, $C_{10}H_8O_3$, melting-point 105° (H. 1898). *L. campestris*, atranorin (Z. 1897). *L. badia*, stereocaulic acid (Z. 1897). *L. effusa*, atarnorin and usnic acid (Z. 1897). *L. subfusca*, atranorin (Z. 1897); (H. 1900). *L. epanora*, zeorin and lepanorin, melting-point 131—132° (Z. 1900), *L. glaucoma* (*L. sordida a-glaucoma*) (from Tyrol), atranorin, thiophanic acid, roccellic acid (Z. 1903). *L. sulphurea*, usnic acid (Z. 1903). *L. parella* ("light crottle"), parellic acid, lecanoric acid (Schunck, Annalen, 54, 257, 274; 41, 161). *L. tartarea* (Linn.) (*Patellaria tartarea*, *Parmelia tartarea*), erythric acid, synonymous with Nees. v. Esenbeck's "remarkable resin" (Brandes' Archiv. Apoth., 16, 135), with Heeren's erythrin, and with Kane's erythrilin (Schweiggers, J. Ch. Phys., 59, 313). Schunck found crustaceous lichens belonging to *Lecanora*, etc., collected on the basalt rocks of the Vogelsberg in Upper Hessia to contain lecanoric and erythric acids (Annalen, 41, 157). In a specimen from Norway, Stenhouse (*ibid.*, 70, 218) found gyrophoric acid. *L. ventosa*, usnic acid (Knop, *ibid.*, 49, 122).

Rhizocarpon geographicum, Dl. (*Lecidea geographica*), usnic acid (Knop, *loc. cit.*). *Lecidea candida* (*Psora candida*), calcium oxalate (Braconnot, Ann. Chim. Phys., [ii.], 28, 319). *L. cineroatra*, lecidic acid, $C_{22}H_{27}O_4.COOMe$, melting-point 147°, and lecidol, melting-point 93° (H. 1898). *L. sudetica*, salazinic acid (Z. 1899). *L. confluens*, confluetin, melting-point 147—148° (Z. 1899). *L. grisella*,

gyrophoric acid (H. 1900). *L. agloeotera* (*L. armeniaca*, var. *lutescens*), roccellic and cetraric acids (Z. 1904).

Lepraria latebrarum, leprarin, melting-point 155°, roccellic acid (Z. 1897), and atranorin (Z. 1900); *d*-usnic, hydroroccellic, lepraric, and talebraic acids (melting-point 208°), and atranorin (H. 1903). *L. flava*, calycin, pinastric acid, calyciarin (Z. 1905). *L. xanthina* (from Vorarlberg), physcion (H. 1906). *L. latebrarum* (Baden-Baden), atranorin, leprariaic acid, oxyroccellic acid, and neobraic acid (H. 1906). *L. candelaris*, calycin (Z. 1906). *L. chlorina*, calycin (Z. 1895).

Lepra candelaris (*Lepraria flava*), calycin, $C_{16}H_{11}O_4 . OH$, melting-point 240—242° (H. 1898).

Leprantha impolita (*Arthonia pruinosa*), lecanoric acid, lepranthin, $C_{26}H_{40}O_{10}$, melting-point 183°, lepranthaic acid, $C_{20}H_{32}O_2$, melting-point 111—112° (Z. 1904).

Mycoblastus sanguinarius, caperatic acid and atranorin (Z. 1899).

Menegazzia pertusa (*Parmelia pertusa*), atranorin and farinacic acid (capraric and pysodic acids absent) (H. 1907).

Nephroma arcticum, zeorin, nephrin, and *d*-usnic acid (Z. 1909). *N. antarcticum*, zeorin and *d*-usnic acid (Z. 1909). *N. parile*, zeorin and mannitol (Z. 1909). *N. resupinatum*, mannitol (Z. 1909). *N. lævigatum*, mannitol (Z. 1909). *Nephromium lævigatum*, usnic acid and nephrin, $C_{20}H_{22}$, H_2O, melting-point 168° (H. 1898). *N. tommentosum*, usnic acid and nephrin (H. 1898). *N. lusitanicum*, nephrin and nephromin, $C_{16}H_{12}O_6$, melting-point 196° (H. 1898).

Ochrolechia androgyna (*Lecanora subtartarea*), gyrophoric acid and calyciarin (Z. 1905). *O. pallescens*, var. *parella* (from Auvergne), parellic acid and ochrolechiasic acid, $C_{22}H_{14}O_9$, melting-point 282° (H. 1906); but no lecanoric acid (see Schunck, Annalen, 1845, 54, 274) (Z. 1898). *O. tartarea*, gyrophoric acid (Z. 1898).

Pannaria lanuginosa, hydroxyroccellic acid, $C_{17}H_{32}O_5$, melting-point 128°, and pannaric acid, $C_9H_8O_4$, melting-point 224° (H. 1901).

Parmelia aleurities, atranorin (Z. 1897). *P. tiliacea*, atranorin and parmelialic acid, melting-point 165° (Z. 1897); the latter is in reality lecanoric acid (H. 1898 and 1900). *P. perlata*, atranorin and hæmatommic acid (Z. 1897); usnic acid, lecanoric acid, and perlatin (H. 1900); imbricaric acid (Z. 1902); no lecanoric acid (H. 1903); atranorin and perlatic acid, $C_{27}H_{27}O_9 . OMe, 2H_2O$ (H. 1904). *P. perlata* from certain sources: (*a*) atranorin, (*b*) atranorin, usnic, and vulpic acids, (*c*) atranorin and lecanoric acid, (*d*) atranorin and perlatin $C_{19}H_{14}O_5(OMe)_2$ (H. 1898). *P. saxatilis*, var. *sulcata*, atranorin and stereocaulic acid (Z. 1897);

protocetraric acid only (H. 1900), not protocetraric but pannatic acid (H. 1904); usnic acid (Schmidt, Annalen, 51, 29). *P. saxatilis*, var. *panniformis*, atranorin, protocetraric acid, and usnetic acid, $C_{24}H_{26}O_8$ (not $C_9H_{10}O_3$), melting-point 192° (H. 1900). *P. saxatilis retiruga*, atranorin, protocetraric acid, and saxatic acid, $C_{25}H_{40}O_8$, melting-point 115° (H. 1903). *P. physodes* (or *P. ceratophylla*, var. *physodes*) is known as "dark crottle," and is employed for dyeing a brown colour on homespun woollen yarn. Contains physodin and two colourless substances (Gerding, Brandes, Arch. Pharm., [ii.], 87, 1), ceratophyllin (H. Annalen, 119, 365); atranorin, physodalic acid, and physodalin (Z. 1897 and 1898); evernuric acid, physodylic acid, capraric acid, and atranorin (H. 1907). *P. parietina*, chrysophanic acid (Rochleder and Heldt); identical with Thomson's (Edin. New Phil. Jour., 37, 187) parietin, also (H. 1895) physcion, $C_{16}H_{12}O_5$, physcianin, $C_{10}H_{12}O_4$, melting-point 143°, and physciol, $C_7H_8O_3$, melting-point 107°. A variety of *P. parietina* growing on sandstone rock and not on trees like that of Rochleder and Heldt, contained vulpic acid (chrysopicrin), (Stein, J. pr. Chem., [i.], 93, 366). *P. caperata* ("stone crottle"), emulsin (Hérissey, J. Pharm., [vi.], 7, 577); capraric acid, $C_{22}H_{18}O_8(COOH)_2$, melting-point 240°, usnic acid, caperatic acid, COOMe, $C_{18}H_{32}O_2(COOH)_2$, melting-point 132°, and caperin, $C_{36}H_{60}O_3$, melting-point 243° (H. 1898), *d*-usnic acid (H. 1900). *P. caperata* from *Castanea vesca*, usnic, capraric and caperatic acids (H. 1904). *P. conspersa*, usnic acid, zeorin, and atranorin (Z. 1898); usnic acid and salazinic acid (H. 1898); *d*-usnic acid and conspersaic acid, melting-point 252° (H. 1903). *P. acetabulum*, atranorin (Z. 1898); atranorin and salazinic acid (H. 1901). *P. excrescens*, zeorin and atranorin (Z. 1898). *P. perlata*, var. *exrescens*, atranorin (Z. 1898). *P. Nilgherrensis*, atranorin (Z. 1898). *P. perforata*, zeorin and atranorin (Z. 1898); lecanoric acid (H. 1900). *P. olivetorum*, atranorin (Z. 1898); lecanoric acid, but no erythric acid (H. 1900); olivetoric acid, $C_{27}H_{34}O_8$, melting-point 141—142° (Z. 1902); atranorin, olivetorin, melting-point 143°, and olivetoric acid, $C_{21}H_{26}O_7$ (H. 1903). *P. pertusa*, physodalic acid (Z. 1898). *P. fuliginosa*, atranorin and lecanoric acid (H. 1898). *P. fuliginosa*, var. *ferruginascens*, lecanoric acid (Z. 1899). *P. pulverulenta*, unknown acid (H. 1898). *P. ciliaris*, everninic acid and atranorin (?) (H. 1898). *P. omphalodes* (*P. saxattilis*, var. *omphalodes*). Under the name of "black crottle" this lichen is employed for dyeing a brown colour in the outer Hebrides (Lewis and Harris); contains stereocaulic acid (Z. 1899). *P. tiliacea*, var. *scortea*, lecanoric acid (Z. 1899). *P. verruculifera*, lecanoric acid

(Z. 1899). *P. glomellifera*, glomelliferin, melting-point 143—144° (Z. 1899 and 1902). *P. incurva*, usnic acid (Z. 1900). *P. Borreri*, lecanoric acid (Z. 1900). *P. sorediata*, diffusin (Z. 1900); lecanoric acid (H. 1900). *P. tinctorum*, atranorin (H. 1900). *P. tinctorum* (E. Africa), atranorin and lecanoric acid (H. 1906). *P. tinctorum* (Madras cinchona bark), atranorin and lecanoric acid (H. 1904). *P. glabra*, lecanoric acid (H. 1902). *P. lacarnensis*, imbricaric acid (Z. 1902). *P. sinuosa*, *d*-usnic and usnaric acids (Z. 1902).

Parmelia cetrata (Java cinchona bark), cetrataic acid, $C_{32}H_{24}O_{14}$, melting-point 178—180° (H. 1903). *P. olivacea*, oliveacein, $C_{17}H_{22}O_6 . H_2O$, melting-point 156°, and oliveaceic acid,

$$C_{16}H_{19}O_5 . OMe,$$

melting-point 138° (H. 1903). *P. revoluta*, atranorin and gyrophoric acid (Z. 1905). *P. pilosella*, atranorin and pilosellic acid, melting-point 245° (Z. 1905). *P. Moügeotti*, *d*-usnic acid (H. 1906).

Peltigera aphthosa, peltigerin, $C_{21}H_{20}O_8$ (or $C_{16}H_{16}O_6$), melting-point 170—180°, and mannitol (Z. 1909). *P. malacea*, peltigerin, zeorin, and mannitol (Z. 1909). *P. horizontalis*, peltigerin, zeorin, and mannitol (Z. 1909). *P. polydactyla*, peltigerin, mannitol, polydactylin, melting-point 178—180°, and peltidactylin, melting-point 237—240°. *P. venosa*, peltigerin. *P. scabrosa*, peltigerin. *P. propagulifera*, peltigerin and zeorin. *P. lepidophora*, peltigerin. *P. praetextata*, mannitol. *P. rufescens*, mannitol. *P. spuria*, mannitol. *P. canina*, caninin (Z. 1909); emulsin (Hérissey, J. Pharm. Chim., [vi.], 7, 577).

Pertusaria amara (*P. communis β-variolosa*, *Variolaria amara*), emulsin (Hérissey, *loc. cit.*); cetraric acid, pertusaric acid, $C_{24}H_{28}O_6$, melting-point 103°, pertusarin, $C_{30}H_{50}O_2$, melting-point 235°, pertusarene, $C_{60}H_{100}$, melting-point 286°, and pertusaridin (H. 1898); salazinic acid and picrolichenin (Z. 1900); orbiculatic acid, $C_{22}H_{26}O_7$ (H. 1901). *P. lactea*, lecanoric acid and variolaric acid, melting-point 285° (Z. 1902). *P. lactea* (sterile Auvergne), lecanoric acid and ochrolechiasic acid (H. 1906). *P. corralina* (*P. ocellata β-coralline*), ocellatic acid, $C_{20}H_{15}O_{11} . OMe$, melting-point 208° (H. 1901). *P. rupestris* (*P. communis β-areolata*), areolatin, $C_{11}H_7O_6 . OMe$, melting-point 270°, areolin, melting-point 243°, and gyrophoric acid, $C_{16}H_{14}O_7$ (H. 1903). *P. glomerata* (Wildbad), porin, $C_{42}H_{67}O_9OMe$, melting-point 166°, and porinic acid $2[C_{11}H_{12}O_4]$, H_2O, melting-point 218° (H. 1903). *P. Wulfenii* (*P. sulfurea*, *P. sulphurella*, *P. fallax*), thiophanic acid (Z. 1904). *P. lutescens*, thiophanic acid (Z. 1904).

Placodium gypsaceum, squamaric acid and usnic acid (Z. 1898);

parellic acid, but no usnic acid (H. 1901). *P. chrysoleŭcăm*, usnic acid (Z. 1898). *P. saxicolum*, var. *vulgare*, usnic acid and zeorin (Paternó, Atti. R. Accad. Lincei, 1876, [ii.], 3); zeorin, but no atranorin (H. 1898), *d*-usnic acid (H. 1900). *P. saxicolum*, var. *compactum*, atranorin (H. 1901). *P. melanaspis*, atranorin (Z. 1898). *P. Lagascoe*, psoromic and usnic acids (Z. 1897).

Placodium crassum, atranorin (trace), *l*-usnic acid (H. 1901). *P. circinatum* (*a*) *radiosum*, salazinic acid (H. 1902).

Physcia ciliaris, emulsin (Hérissey, J. Pharm. Chim., [vi.], 7, 577). *P. endococcina*, zeorin and atranorin (Z. 1895), rhodophyscin and endococcin (Z. 1905). *P. caesia*, zeorin and atranorin (Z. 1895); atranorin and zeorin (H. 1902). *P. stellaris*, *f. adscendens*, atranorin (Z. 1895). *P. parietina*, atranorin and placodin, melting-point 245° (H. 1899). *P. medians*, vulpic acid and calycin (Z. 1895), calycin and callopismic acid (Z. 1897). *P. pulverulenta*, var. *β-pityrea*, atranorin (Z. 1895).

Physcia tenella, atranorin (Z. 1895). *P. aipolia*, atranorin (Z. 1895).

Cetraria glauca (*Platysma glaucum*), atranorin and caperatic acid (Z. 1899). *Cetraria cucullata* (*P. cŭcŭllatum*), lichenostearic acid and usnic acid (Z. 1899). *P. diffusum*, diffusin, melting-point 135—136°, and usnic acid (Z. 1899).

Pleopsidium chlorophanum, rhizocarpic acid (Z. 1895).

Pseudevernia ericetorum, atranorin, physodalin (Z. 1905).

Psora ostreata, lecanoric acid (Z. 1899).

Pulveraria chlorina, calycin, vulpic acid, and lepraric acid, melting-point 228° (H. 1898). *P. latebrarum*, atranorin, parellic acid, latebride, melting-point 128°, and pulverin, melting-point 262° (H. 1898). *P. farinosa*, oxyroccellic acid, and pulveraric acid, melting-point 234° (H. 1898).

Raphiospora flavovirescens, rhizocarpic acid (Z. 1895).

Ramalina calicaris, var. *fastigiata*, contains large quantities of starch (lichenin) and a small quantity of saccharic acid (Berzelius, Scherer's Annalen, 3, 97), usnic acid (Rochleder and Heldt, *ibid.*, 48, 9). *R. calicaris*, var. *fraxinea*, lichenin and usnic acid (Rochleder and Heldt, *loc. cit.*); *a*-usnic acid (Hesse, Annalen, 117, 297). *R. ceruchis*, usnic acid and usnaric acid (H. 1898). *R. armorica*, atranorin, armoricaic acid, melting-point 240—260°, armoric acid, $C_{18}H_{18}O_7$, H_2O, melting-point 226—228° (H. 1907). *R. cuspidata*, cuspidatic acid, $C_{16}H_{20}O_{10}$, melting-point 218° (H. 1900). *R. farinacea*, *d*-usnic acid and ramalic acid, melting-point 240—245° (H. 1903). *R. subfarinacea*, *d*-usnic acid and salazinic acid

(Z. 1907). *R. minuscula*, *d*-usnic acid (Z. 1907). *R. Kullensis*, *d*-usnic acid, kullensisic acid, $C_{22}H_{18}O_{12}$ (Z. 1907). *R. obtusata*, *d*-usnic acid, ramalinellic acid, melting-point 169°, and obtusatic acid (Z. 1907). *R. Landroënsis*, *d*-usnic acid and landroënsin (Z. 1907). *R. pollinaria*, ramalic acid, $C_{16}H_{12}O_3OMe$, and evernic acid (Z. 1897); usnic acid, atranorin, evernic acid, and ramalic acid (H. 1898). *R. fastigiata*, emulsin (Hérissey, J. Pharm. Chim., 1898, [vi.], 5, 577). *R. fraxinea*, emulsin (Hérissey, *ibid.*). *R. polymorpha*, usnic acid (Z. 1897). *R. scopulorum* (see Thomson, Annalen, 53, 252), *d*-usnic acid, scopuloric acid, $C_{18}H_{16}O_9$, melting-point 260° (Z. 1907). *R. thraulsta*, usnic acid (Z. 1900). *R. yemensis*, *d*-usnic acid (H. 1902).

Reinkella birellina, roccellic and oxyroccellic acids (H. 1898).

Rhizocarpon geographicum f. contiguum, parellic acid, rhizonic acid, $C_{19}H_{20}O_7$, melting-point 185°, rhizocarpic acid, $C_{28}H_{22}O_7$ (H., Ber., 1898, 31, 663), rhizonic acid is $OMe.C_{17}H_{14}O_2(OH)_2COOH$ (H.).

R. geographicum f. lecanorinum, rhizocarpic acid (Z. 1895); parellic acid, rhizocarpinic acid, melting-point 156°, rhizocarpic acid,

$$COOH.C_{24}H_{16}O_2.COOEt,$$

melting-point 177—178°. Parellic acid,

$$COOMe.C_{17}H_{11}O_3(COOH)_2,$$

melting-point 262—265°, is the same as Zopf's psoromic acid, and the squamaric acid and zeoric acid of other writers (H.). *R. geographicum f. geronticum*, parellic and rhizocarpic acids, but not rhizocarpinic acid (H., 1909).

Rhizoplaca opaca (*Lecanora chrysoleuca*, *β-opaca*, *Parmelia rubina*, *β-opaca*, *Squamaria chrysoleuca β-opaca*), usnic acid, placiodilic acid (previously termed placiodilin), rhizoplacic acid, $C_{21}H_{40}O_5$, melting-point 94—95° (Z. 1905), usnic acid and placiodilic acid, $C_{17}H_{18}O_7$, melting-point, 156—157° (Z. 1906).

Roccella fuciformis (*R. tinctoria*, var. *fuciformis*). This well-known "orchella weed" is imported from Angola, Zanzibar, Madagascar, Ceylon, and Lima for the purpose of manufacturing archil and cudbear. It contains erythric acid (Heeren's erythrin, Kane's erythrilin) and roccellic acid (Schunck, Pharm. J., [iii.], 39, 164; Annalen, 61, 64; Kane, Trans. Roy. Soc., 1840, 273; Heeren and Schweiggers, J. Pharm. Chim., 59, 346). Stenhouse (Annalen, 149, 288) examined a Lima weed in 1848, and found it to contain lecanoric acid, but this was probably *R. tinctoria* and not identical with the *R. fuciformis* examined by him in 1869, and in which he found

erythric acid. Cf. Hesse (Annalen, 117, 329, and 139, 22) who found Lima weed to contain erythric acid, but not lecanoric acid. Stenhouse considers the *R. Montagnei* from Angola, in which he found erythric acid to be identical with *R. tinctoria*, var. *fuciformis*, examined by Schunck. A stunted variety of *R. fuciformis*, examined by Menschutkin and Lamparter, contained β-erythrin. In a better growing specimen erythrin was obtained (Lamparter, Annalen, 134, 243). A variety of *R. fuciformis*, probably from the west coast of Africa, contained erythric acid and a bitter substance picroroccellin (Stenhouse and Groves, *ibid.*, 185, 14). More recently Hesse (1898) has found the weed to contain erythric acid and oxyroccellic acid.

Roccella Montagnei, erythric acid and oxyroccellic acid (H. 1898); orcinol (Ronceray, Bull. Soc. Chim., 1904, [iii.], 1097). *R. fruticosa*, erythric acid (erythrin) (H., Ber., 1904, 37, 4693). *R. phycopsis* (Crete), erythrin, oxyroccellic acid, oxalic acid, and erythritol (H. 1906). *R. peruensis* (*R. fructectosa* and *R. cacticola*), erythrin, oxyroccellic and roccellic acids (H. 1898), erythrin, erythritol and oxalic acid (H. 1906). *R. portentosa*, lecanoric acid (H. 1898). *R. decipiens*, lecanoric acid (H. 1898). *R. sinensis*, lecanoric acid (H. 1898).

Roccella tinctoria.—This lichen, used largely for the manufacture of orchil and cudbear, is imported from the Cape of Good Hope, the Cape Verde Islands, and Chile (Valparaiso weed). Formerly it seems to have been imported also from Lima (Stenhouse). It contains lecanoric acid (Stenhouse's α- and β-orsellic acid) and roccellimin. The latter is, however, probably a decomposition product of the former (Stenhouse, Annalen, 68, 55; 149, 288; Phil. Mag., [iii.], 32, 300). According to Hesse (1898) it contains erythrin, oxyroccellic acid, roccellic acid, and lecanoric acid, whereas Ronceray (Bull. Soc. Chim., 1904, [iii.], 31, 1097) detected in this lichen the presence of lecanoric acid and orcinol (cf. Hesse, Ber., 1904, 37, 4693).

Roccellaria intricata, zeorin and roccellaric acid, melting-point 110° (H. 1898).

Squamaria elegans (*Gasparrinia elegans*), chrysophanic acid (Thomson, Phil. Mag., [iii.], 25, 39); physcion (H.).

Solorina crocea, soloric acid, melting-point 199—201° (Z. 1895).

Sphærophorus fragilis, sphærophorin, melting-point 138—139°, and fragilin (Z. 1898), sphærophorin $(C_{14}H_{16}O_4)_n$ or $C_{28}H_{24}O_8$, sphærophoric acid, melting-point 206—207°, and fragilin (Z. 1905).

Sphyridium placophyllum, atranorin (Z. 1898).

Stereocaulon alpinum, atranorin, and stereocaulic acid, melting-point 200—201° (Z. 1895). *S. corallöides*, atranorin and psoromic acid (Z. 1895), usnetic acid, atranorin, and an acid not psoromic acid. Zopf's stereocaulic acid from *S. alpinum* is usnetic acid (H. 1900). *S. incrustatum*, atranorin and psoromic acid (Z. 1895). *S. vesuvianum*, psoromic acid (Z. 1895). *S. denudatum*, var. *genuinum*, atranorin (Z. 1895). *S. tomentosum*, atranorin (Z. 1895). *S. pileatum*, atranorin and stereocaulic acid (Z. 1895 and 1899). *S. condensatum*, atranorin (Z. 1895). *S. paschale*, atranorin (Z. 1895). *S. virgatum* f. *primaria*, atranorin (Z. 1895). *S. ramulosum*, atranorin (Z. 1895). *S. salazinum*, salazinic acid, which blackens at 260—262° (H. 1900).

Sticta fuliginosa, trimethylamine (Z. 1897). *S. aurata*, stictaurin, a derivative of pulvic acid (Z. 1899). Stictaurin has the formula $C_{18}H_{12}O_5$ (H. 1900). *S. desfontainii*, calycin and ethyl-pulvic acid (H. 1900). *S. pulmonaria*, stictaic acid, $C_{18}H_{11}O_8(OMe)$, melting-point 264°, stictinic acid (Knop and Schnedermann, J. pr. Chem., 1846, 39, 365), and not protocetraric acid (H. 1900). This lichen is known as "hazel crottle".

Stictina gilva, stictinin, melting-point 160—161° (Z. 1905).

Thamnolia vermicularis, thamnolic acid, melting-point 202—204° (Z., Chem. Zentr., 1893, [ii.], 54). According to Hesse this has the formula $C_{19}H_{15}O_{10}$. OMe (1898 and 1900).

Thallœdema candidum, probably lecanoric acid (H. 1898).

Thalloschistes flavicans, parietin (Z. 1905) (Brittany); physcion and acromelin (H. 1907).

Tornabenia chrysophthalma, physcion (H. 1907). *T. flavicans*, var. *crocea*, physcion (H. 1907). *T. flavicans*, var. *acromela* (*Physcia acromela*), acromelin, $C_{17}H_{16}O_9$, melting-point, 242°, and acromelidin, $C_{17}H_{20}O_9$, melting-point 162° (H. 1907). *T. flavicans*, var. *cinerascens*, physcion and acromelin (H. 1907).

Umbilicaria pustulata (*Gyrophora pustulata*), gyrophoric acid, $C_{18}H_{16}O_7$ (?), (Stenhouse, Annalen, 70, 218; Z. 1898; H. 1898).

Urceolaria lichens, collected from the basalt rock of the Vogelsberg in Upper Hessia, contain lecanoric and erythric acids (Schunck, Mem. Chem. Soc., 1, 71).

Urceolaria scruposa, var. *vulgaris*, atranorin and lecanoric acid (H. 1898, 1904, 1907); patellaric acid (Z. 1902). *U. cretacea* (*U. scruposa*, var. *gypsacea*), lecanoric acid, but no atranorin, zeorin, or parmelialic acid (H. 1898; cf. Zopf, 1897).

Usnea barbata (*Lichen barbatus*, *Parmelia barbata*), usnic acid (Rochleder and Heldt, Annalen, 48, 8; Stenhouse, *ibid.*, 155, 51),

and lichenin (Berzelius, Scherer's Annalen, 3, 205; Hesse, Annalen, 137, 241; Ber., 10, 1324), usnic and barbatic acids (H. 1898); emulsin (Hérissey, J. Pharm. Chim., [vi.], 7, 577). *U. barbata* f. *dasypoga*, usnic acid and usnaric acid, $C_{30}H_{22}O_{15}$, melting-point 240—260° (H. 1898), *d*-usnic, usnaric, and alectoric acids (H. 1900); barbatic, usnic, and usnaric acids, but no alectoric acid (Z. 1902); alectoric acid (H. 1903). *U. barbata*, var. *ceratina*, usnic acid, $C_{18}H_{16}O_7$, melting-point 195—196°, and barbatin (H., Annalen, 1895, 284, 157). *U. barbata* α-*florida*, *d*-usnic, usnaric, and parellic acids, and usnarin (H. 1902). *U. ceratina*, usnic acid, barbatic acid and barbatin (H. 1898). *U. ceratina* (Black Forest), barbatic and usnic acids (Z. 1902), *d*-usnic acid, barbatic acid, and barbatin (H. 1903), (Java cinchona bark), *d*-usnic, usnaric, and parellic acids and ceratin (H. 1903). *U. ceratina* β-*hirta* (Bolivian), *d*-usnic, usnaric, p'icatic, and barbatic acids (H. 1903). *U. barbata* (β-) *hirta*, *d*-usnic, usnaric, and barbatic acids, and usnarin (H. 1902), atranorin (H. 1906). *U. barbata* (β-) *hirta* (St. Thomas), *d*-usnic and usnaric acids, and santhomic acid, $C_{11}H_{14}O_4$, melting-point 166° (H. 1902). *U. hirta*, usnic acid (Knop, Annalen, 49, 103), usnic acid, alectoric acid, hirtic acid, melting-point 98°, and hirtellic acid (melting-point 215° decomp.), (Z. 1903). *U. cornuta*, *d*-usnic and usnaric acids (Z. 1902). *U. longissima*, barbatic and usnic acids (Z. 1897; H. 1898). *U. longissima* (from Amani), ramalic acid, *d*-usnic acid, and dirhizonic acid, $C_{18}H_{16}O_5(OMe)_2$, melting-point 189° (H. 1906). *U. florida*, usnic acid (Knop, Annalen, 49, 103); usnic acid and hirtellic acid (Z. 1904). *U. schraderi*, *d*-usnic acid and usnaric acid (Z. 1905). *U. microcarpa*, *d*-usnic acid and usnaric acid (Z. 1905). *U. articulata*, var. *intestiniformis* (Indian cinchona bark), *d*-usnic acid, barbatic acid, and articulatic acid, $C_{18}H_{16}O_{10}$ (?), (H. 1907). *U. plicata*, *d*-usnic acid, usnaric acid, usnarin, and plicatic acid, $C_{20}H_{22}O_8(OMe)$, melting-point 133° (H. 1900). *U. scrŭposa*, atranorin and lecanoric acid (Z. 1902).

Pertusaria dealbata, Nyl. (*Variolaria dealbata*, *Lichen dealbatus*), variolarin (Robiquet, Annalen, 42, 236; 58, 320). Schunck found crustaceous *Variolaria* collected on the basalt rocks of the Vogelsberg in Upper Hessia, to contain lecanoric and erythric acids.

Xanthoria parietina (*Parmelia parietina*, *Physcia parietina*), atranorin and physcion (H. 1898). *X. lychnea*, physcion (H. 1898). *X. candelaria* (*X. controversa*, *X. lychnea*, var. *pygmæa X. parietina*, var. *lychnea*), parietin, melting-point 202° (Z. 1904).

Orsellinic Acid.

Orsellinic acid, $C_8H_8O_4$, H_2O, was first prepared by Stenhouse (Annalen, 68, 61) by digesting lecanoric acid with boiling baryta water, and can also be produced from erythrin in a similar manner. According to Hesse (*ibid.*, 139, 35), the solution of erythrin in baryta water is heated on the steam-bath until a sample of the product no longer yields a gelatinous precipitate when neutralised with hydrochloric acid. The liquid is then acidified, and the orsellinic acid, which separates on standing, is crystallised from alcohol or acetic acid.

Orsellinic acid crystallises from dilute acetic acid in needles with $1H_2O$. When heated, it melts at 176° with evolution of carbon dioxide and formation of orcin, and is evidently an orcin carboxylic acid.

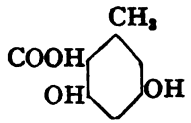
Ethyl orsellinate, $C_{10}H_{12}O_4$, colourless leaflets, melting-point 132°, is produced when erythrin is boiled for several hours with alcohol (Stenhouse, *loc. cit.*), and can be prepared in an identical manner from lecanoric acid (Schunck, Annalen, 54, 265).

Methyl orsellinate, $C_9H_{10}O_4$ (Schunck, *loc. cit.*, and Stenhouse, *loc. cit.*), and iso*amyl orsellinate*, $C_{13}H_{18}O_4$ (Stenhouse; Hesse, Annalen, 139, 37), melting-point 76°, have also been obtained.

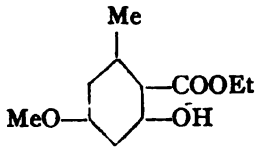
According to Heinrich (Ber., 1904, 37, 1406), ethyl orsellinate in alkaline solution reacts with diazobenzene chloride with formation of the disazobenzene derivative, $C_6Me(OH)_2(C_6H_5N_2)_2COOEt$, red needles, melting-point 186°, and this, on reduction with stannous chloride and hydrochloric acid and further heating with hydrochloric acid at 160° gives diamino-orcin hydrochloride,

$C_6HMe(OH)_2(NH_2)_2(Me:(NH_2)_2:(OH)_2 = 1:2:4:3:5$.

The constitution of orsellinic acid is therefore to be represented as follows:—

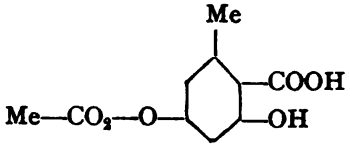


This structure is supported by the conductivity measurements of Thiel, Schumacher, and Roemer (Ber., 1905, 38, 3860), and further by the work of Fischer and Hoesch (Annalen, 1912, 391, 347). These last authors treated methyl-orsellinate with an ethereal solution of diazomethane—which methylates phenol carboxylic acids preferentially in the para-position—and thereby obtained an *α-methyl ether*—

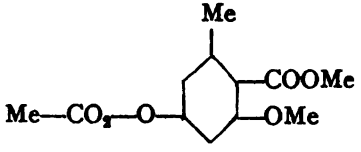


melting-point 72—75° C., which gave a red-violet ferric chloride reaction.

When orsellinic acid was treated with methyl-chlorocarbonate in cold N caustic soda—a reagent which also preferentially attacks the para-position—the product of the reaction was *methyl-carbonato-orsellinic acid*—

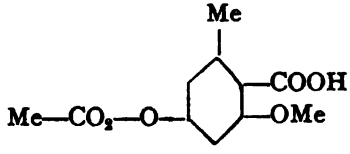


(5-methyl-carbonato-3-hydroxy-o-toluic acid), melting-point 153—154° C. (corr.), which also gave a characteristic coloration with ferric chloride, whereas the product of the action of ethereal diazomethane on this last substance was *methyl-carbonato-orsellinate-β-methyl ether*—

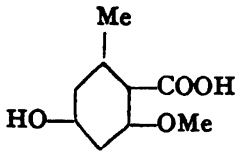


melting-point 86° C. (corr.), which gave no coloration with ferric chloride.

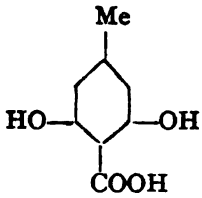
On hydrolysis of this ester with concentrated sulphuric acid at 25° C., *methyl-carbonato-orsellinic-acid-β-methyl ether*—



melting-point 145° C. (corr.), was obtained, which also failed to develop a coloration with ferric chloride, whereas, when this was further hydrolysed by means of caustic soda, it yielded *orsellinic acid-β-methyl ether*—

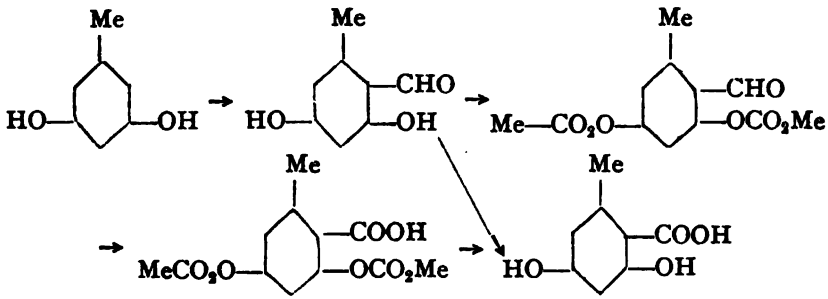


which decomposes at 175° C., and develops a yellow-red coloration with ferric chloride. As Fischer and Hoesch point out, were the older formula for orsellinic acid correct—



the β-methyl ether would be a derivative of salicylic acid, and should develop its characteristic colour with ferric chloride, and moreover, the α and β-methyl ethers would be identical, whereas they are undoubtedly isomeric.

The constitution thus arrived at has been substantiated by the synthesis of orsellinic acid by Hoesch (Ber., 1913, 46, 886), who obtained it by oxidation of orcyl-aldehyde—prepared from orcine by Gattermann's method—or, more readily, of its dimethylcarbonato, or diethylcarbonato derivatives, followed by hydrolysis of the resulting acid with N caustic soda solution. The synthesis may be represented thus:—



An attempt to prepare this acid from orcinol by a method analogous to that used for the preparation of salicylic acid from phenol was unsuccessful.

Dimethylcarbonato-orcyl aldehyde, needles, melting-point 84—85°, according to Hoesch becomes yellow on exposure to light.

Monomethylcarbonato-orcyl aldehyde, prisms, melts at 79°, *diethylcarbonato-orcyl aldehyde*, needles, at 60°, and *diethylcarbonato-orsellinic acid*, prisms, at 112° (decomp.).

Lecanoric Acid.

Lecanoric acid (*Diorsellinic acid*), $C_{16}H_{14}O_7$, H_2O, was first described by Schunck under the name of "lecanorin," and was isolated by him from various species of the *Lecanora* and *Variolaria* lichens. It is also present in some quantity in the *Rocella canariensis*, *R. portentosa*, *R. sinensis*, and *Parmelia perlata* (*loc. cit.*), and, according to Hesse (Annalen, 139, 24), is best isolated by the following method, which is a modification of that originally devised by Schunck. The finely divided lichen is extracted with ether, the extract evaporated, and the greenish-white crystalline residue treated with lime water. The solution, when neutralised with acid, gives a precipitate of lecanoric acid, which is collected and crystallised from alcohol. In case the product is not quite pure it is treated with ether, which dissolves the acid, but not the impurity.

Lecanoric acid crystallises in colourless needles, melting-point 166° (Hesse, Ber., 37, 4693), the solutions of which possess an acid reaction. With alcoholic ferric chloride it gives a dark purple coloration, and with dilute calcium hypochlorite a blood-red liquid, which, according to Hesse, is characteristic, and can be used to distinguish this substance from the known lichen acids.

Dibromolecanoric acid (Hesse, Annalen, 139, 28), $C_{16}H_{12}O_7Br_2$, consists of minute prisms, melting-point 179°, whereas *tetrabromolecanoric acid*, $C_{16}H_{10}O_7Br_4$, prisms, melts at 157°.

Potassium lecanorate, $C_{16}H_{13}O_7K$, H_2O; *barium lecanorate*, $(C_{16}H_{13}O_7)_2Ba$, $5H_2O$; *calcium lecanorate* $(C_{16}H_{13}O_7)_2Ca$, $4H_2O$; *silver lecanorate*, $C_{16}H_{13}O_7Ag$; *lead lecanorate*,

$$(C_{16}H_{13}O_7)_2Pb + PbH_2O_2;$$

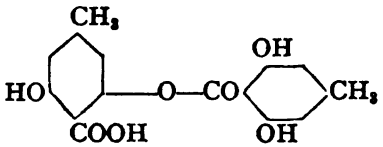
and *copper lecanorate* $(C_{16}H_{12}O_7)_2Cu$, $2H_2O$, have been obtained (J. pr. Chem., [ii.], 57, 264).

When boiled with water lecanoric acid yields *orsellinic acid*, $C_{16}H_{14}O_7 + H_2O = 2C_8H_8O_4$; whereas by means of boiling acetic acid or baryta water, orcin and carbon dioxide are simultaneously produced: $C_{16}H_{14}O_7 + H_2O = C_8H_8O_4 + CO_2 + C_7H_8O_2$.

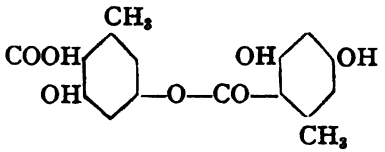
On the other hand, methyl alcohol at 85° gives, in addition to orcin and carbon dioxide, *orsellinic acid methyl ester*—

$$C_{16}H_{14}O_7 + CH_3OH = C_7H_7O_2 . COOCH_3 + C_7H_8O_2 + CO_2$$

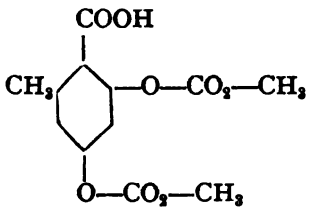
The constitution originally assigned to lecanoric acid—



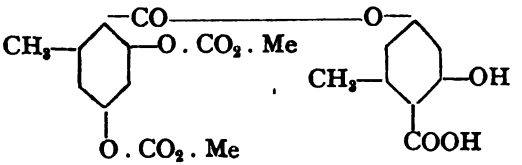
in view of the work of. Heinrich (Ber., 37, 1406) on orsellinic acid, is more accurately expressed as follows :—



This structure has been confirmed by the synthesis of the acid (Fischer and Fischer, Ber., 1913, 46, 1138). These authors converted *dimethyl-carbonato-orsellinic acid*—



into its chloride (melting-point 53—56° C.) by the action of phosphorus pentachloride in presence of acetone, dissolved the product in the same solvent and gradually added a well-cooled solution of orsellinic acid in acetone and N aqueous sodium hydrate, whereby *dimethyl-carbonato-orsellinoyl-orsellinic acid*—



needles, melting-point 185—187° C., was formed. When hydrolysed by means of aqueous caustic soda, this slowly passed into lecanoric

acid, colourless needles, which softens at 170°, and is completely melted at 175°, with evolution of gas—cf. Hesse. The crystals when air-dried contain 1 molecule of water of crystallisation.

The identity of the product thus obtained with natural lecanoric acid was established by comparing their melting-points, colour reactions with ferric chloride, and with bleaching powder solution, and finally by converting each into *methyl-lecanorate-trimethyl-ether*, $C_{20}H_{22}O_7$.

The trimethyl-ether of methyl-lecanorate has been shown by Fischer (Ber., 1913, 46, 3253) to be identical with the product of the action of diazomethane on evernic acid. (See below.)

Evernic Acid and Everninic Acid.

Evernic acid, or *lecanoric acid monomethyl ether*, was first isolated by Stenhouse from the *Evernia prunasti* (Annalen, 68, 83), and has been found also by Hesse (Ber., 1897, 30, 366) to exist in the *Ramalina pollinaria* (compare also Zopf, Annalen, 1897, 297, 271).

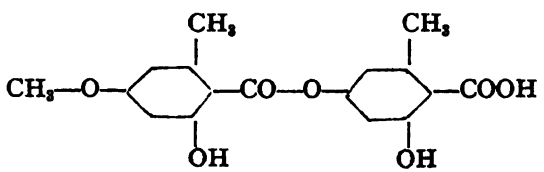
The lichen is extracted with diluted milk of lime, the extract neutralised with acid, the precipitate collected, dried, and digested with a little boiling alcohol. The hot alcoholic liquid, treated with its own volume of water, deposits crystals of evernic acid (Stenhouse).

Evernic acid crystallises in small colourless needles, melting-point 168—169°, readily soluble in hot alcohol, and when boiled with solutions of the alkali hydroxides or baryta water, gives CO_2, orcinol, and *everninic acid*—

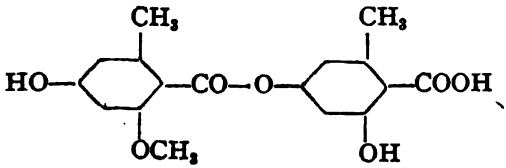
$$C_{17}H_{16}O_7 + H_2O = C_9H_{10}O_4 + C_7H_8O_2 + CO_2$$

Ramalic acid suffers a similar decomposition.

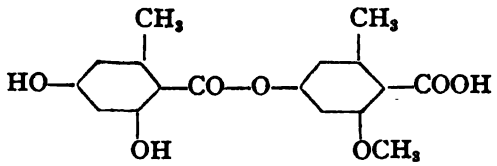
Fischer (Ber., 1913, 46, 3253; and 1914, 47, 505) showed that when evernic acid was methylated by means of diazomethane, in ethereal solution, a neutral crystalline ester identical with trimethyl-lecanoric acid methyl ester was obtained, and he pointed out that, as the methoxy group in everninic acid is in the para-position to the carboxyl group, the structure of evernic acid must be—



From this it follows that ramalic acid may be expressed as—



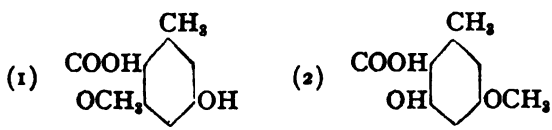
or



For descriptions of the Na, Ba, Ca, Cu, Pb, and Ag, salts of evernic acid, cf. Hesse (J. pr. Chem., 1915, [ii.], 92, 425).

Diacetyl evernic acid, $C_{17}H_{16}O_7Ac_2$, is a crystalline powder, melting-point 144°.

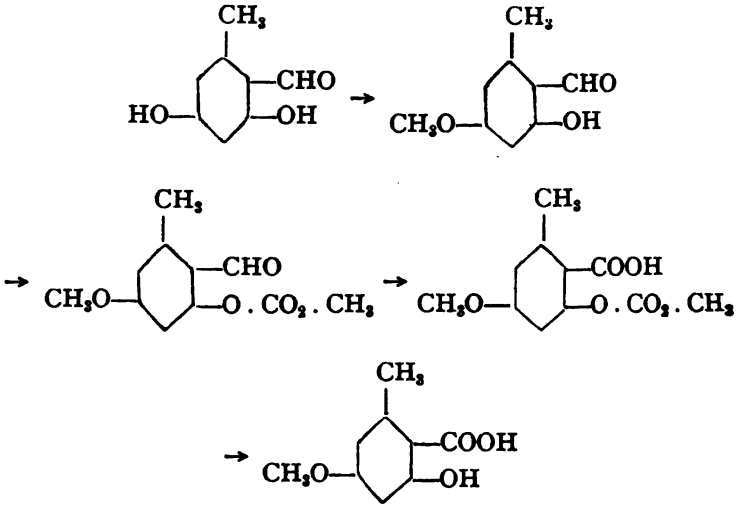
Everninic acid (orsellinic acid monomethyl ether) resembles benzoic acid in appearance, melts at 157°, and yields the ethyl ester $C_9H_9O_4(C_2H_5)$, melting-point 72°. By digestion with hydriodic acid, everninic acid gives orcinol, CO_2, and one molecule of methyl iodide. According to Heinrich (Ber., 1904, 37, 1406), two formulæ are possible for everninic acid :—



Fischer and Hoesch (Annalen, 1912, 391, 347) have, however, shown that *orsellinic acid α-methyl ether*, prepared by them, and which has the structure (2), is identical with everninic acid.

This conclusion has been further substantiated by the synthesis of *everninic aldehyde*, melting-point 65° C. (and from it of everninic acid), by Hoesch (Ber., 1913, 46, 886), by the careful methylation of orcyl aldehyde with methyl sulphate, and 2N caustic soda in presence of acetone. This when treated with an acetone solution of methyl-chlorocarbonate, yielded *methylcarbonato-everninic aldehyde*, needles, melting-point 77° C., and the latter, when oxidised with potassium permanganate, was converted into *methylcarbonato-everninic acid*, needles, decomposing at about 100° C., which on hydrolysis with N caustic soda solution yielded everninic acid.

These changes may be represented thus:—



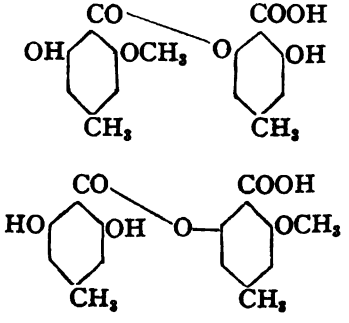
Hesse (J. pr. Chem., 1915, [ii.], 92, 425) has described the following derivatives of everninic acid:—

Acetyl everninic acid, $C_9H_9O_4Ac$, colourless prisms, melting-point 111° C.

Nitro-everninic acid, orange-red needles, melting-point 195° C.

Dinitro-everninic acid, $C_9H_8O_4(NO_2)_2H_2O$, golden-yellow needles, melting-point 87° C.—the potassium salt is very explosive.

Hesse's expression (J. pr. chem., [ii.], 57, 253) of the isomerism of evernic acid and ramalic acid, and which was based upon the older formula of orsellinic acid, is as follows:—

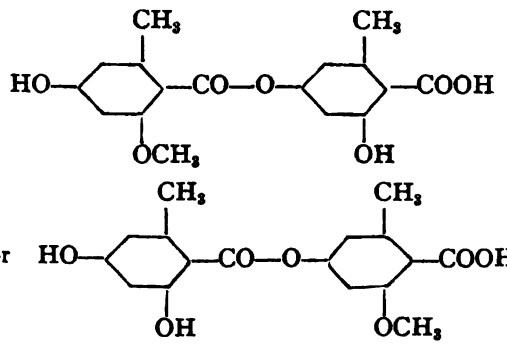


Ramalic Acid.

Ramalic acid (lecanoric acid monomethyl ether), $C_{17}H_{16}O_6OMe$, has been isolated by Hesse, by means of ether, from the lichens *Ramalin pollinaria* (J. pr. Chem., [i.], 57, 253) and *Evernia divaricata* (Ber., 1897, 30, 357). It crystallises in colourless needles, melting-point 179—180° C., and gives with alcoholic ferric chloride a violet coloration. It differs from the isomeric evernic acid, which occurs in conjunction with it, in being sparingly soluble in ether (Zopf, Annalen, 297, 306), but when hydrolysed with baryta water behaves like evernic acid, producing orcin, carbon dioxide, and everninic acid (cf. evernic acid, p. 548).

The anhydrous potassium and barium salts, the latter of which is sparingly soluble, have been prepared and described by Hesse (J. pr. Chem., 1898, [ii.], 57, 232).

As previously stated, the structure of ramalic acid is represented by one of the two following formulæ :—



Erythrin.

Erythrin, erythric acid, erythrinic acid, erythrolecanoric acid, $C_{20}H_{22}O_{10}H_2O$, is a constituent of most lichens from which archil is prepared. It was discovered by Heeren (Schweigger's Journ. f. Chem., 59, 513) in *Rocella tinctoria* (D.C.), from which lichen, and several others of the same genus, it may be extracted by boiling water, or better, with milk of lime (cf. also Kane, Stenhouse, and Hesse (*loc. cit.*); Schunck, Annalen, 61, 69; De Luynes, Ann. Chim. Phys., [4], 2, 385; Menschutkin, Bull. Soc. chim., [2], 2, 424).

The method adopted by Stenhouse to prepare this substance from the *Rocella fuciformis* is as follows (Annalen, 68, 72, and 149, 290): Three pounds of the lichen are macerated for twenty minutes in a milk of lime made by shaking ½ lb. of lime in 3 gallons of water, and

the product filtered by means of a bag filter. The clear liquid, as it passes through, is immediately precipitated with hydrochloric acid, as prolonged contact with the lime decomposes part of the erythrin. The crude erythrin collected on bag filters is freed from acid and calcium chloride by stirring it up once or twice with a considerable quantity of water and again collecting.

Erythrin forms small colourless needles, melting at 148° (Hesse, Ber., 1904, 37, 4693), and not at 164°, as stated by Ronceray (Chem. Zentr., 1904, ii., 1504), and is sparingly soluble in water, easily soluble in alcohol, ether, and alkalis. Alcoholic ferric chloride gives a purple-violet coloration, which passes to brownish-red on addition of excess of the reagent.

When boiled with water, erythrin gives (*a*) *orsellinic acid* and (*b*) *picrcerythrin* (Schunck, Annalen, 61, 65)—

$$C_{20}H_{22}O_{10} + H_2O = (a)\ C_8H_8O_4 + (b)\ C_{12}H_{16}O_7;$$

whereas by boiling with alcohol, picroerythrin and *orsellinic acid ethyl ester* (*c*) are produced (Heeren, *loc. cit.*; Kane, Annalen, 39, 25)—

$$C_{20}H_{22}O_{10} + C_2H_5OH = (c)\ C_8H_7(C_2H_5)O_4 + C_{12}H_{16}O_7$$

With amyl alcohol a similar reaction occurs with formation of (*d*) *amylorsellinate* and picroerythrin (Hesse, Annalen, 139, 22)—

$$C_{20}H_{22}O_{10} + C_5H_{12}O = (d)\ C_8H_7O_4 . C_5H_{11} + C_{12}H_{16}O_7$$

On the other hand, excess of lime water (Lamparter, Annalen, 134, 255) gives orcin, CO_2, and erythrite—

$$C_{20}H_{22}O_{10} + 2H_2O = 2C_7H_8O_2 + 2CO_2 + C_4H_{10}O_4$$

Tribromerythrin, $2C_{20}H_{19}Br_3O_{10}$, $3H_2O$ (Hesse, Annalen, 117, 310; and *ibid.*, 139, 32) consists of white crystalline spherules which cake together a little above 100° and melt at 139°. Boiled with alcohol, it is resolved into *ethyldibromorsellinate* and *brompicroerythrin*.

Picroerythrin or *erythro-orsellinic acid*, $C_{12}H_{16}O_7$, $3H_2O$, forms colourless prisms, melts at 158°, is readily soluble in hot water, and gives with ferric chloride a purple-violet coloration. It appears to be most readily obtained in the pure condition by Hesse's method of boiling erythrin with amyl alcohol (*loc. cit.*).

Digestion with hot baryta water converts picroerythrin into CO_2, orcin, and erythrite—

$$C_{12}H_{16}O_7 + H_2O = CO_2 + C_7H_8O_2 + C_4H_{10}O_4$$

The experiments of De Luynes, Menschutkin, and Hesse have confirmed the view first put forward by Berthelot, that erythrin is

the *monolecanoric ester*, and picroerythrin the *monoorsellinic ester* of *erythrite*.

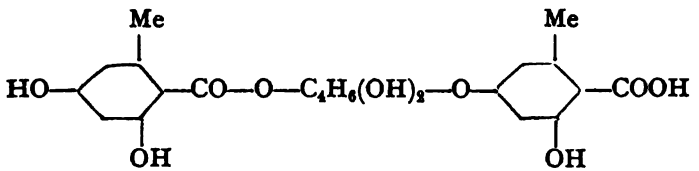
According to Hesse (Ber., 1904, 37, 4693; J. pr. Chem., 1906, [ii.], 73, 113), erythrin contains a free carboxyl group, and must therefore be represented as follows:—

$$C_4H_6(OH)_2 . O . C_6H_2(OH) . CO . O . C_6H_2(OH)COOH$$
$$\qquad\qquad\qquad\quad |\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad CH_3\qquad\qquad\qquad CH_3$$

whilst picroerythrin has the formula—

$$O . CH_2(CH . OH)_2 . CH_2OH$$
$$|$$
$$C_6H_2(OH)COOH$$
$$|$$
$$CH_3$$

On the other hand, Zerner (Monatsh., 1914, 35, 1021) considers that the structure of erythrin is best represented thus—



β-Erythrin, $C_{21}H_{24}O_{10}$, can be prepared by the action of lime water on some varieties of the *R. fuciformis* (Menschutkin, *loc. cit.*). It is a white crystalline powder; melting-point 115—116° (Lamparter, *loc. cit.*); nearly insoluble in water, and dissolves in alcohol and ether with violent evolution of CO_2. Boiled with water, orsellinic acid and β-picroerythrin are produced; with alcohol, the latter body together with ethylorsellinate.

10. *β-Picroerythrin*, $C_{13}H_{16}O_{10}$, crystallises in needles, very soluble in water and alcohol. With boiling baryta water it is resolved into CO_2, erythrite, and β-orcinol (Menschutkin).

According to Hesse (*loc. cit.*), it is probable that β-erythrin is not a chemical individual, but consists mainly of erythrin, the properties of which are modified by the accompanying impurities.

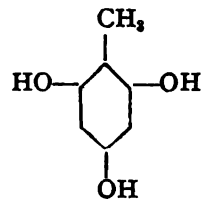
Atranorin.

Atranorin, $C_{19}H_{18}O_8$, is present in the lichens *Evernia vulpina*, *E. prunastri*, *E. furfuracea*, *Lecanora atra*, *L. sordida*, *Parmelia perlata*, *P. physodes*, *P. tinctorium*, *Physcia stellaris*, *Xanthoria parietina*,

Cladonia rangiformis, *Stereocaulan vesuvianum* and others. It forms colourless prisms, melting-point 195—197° C. (Zopf), 187—188° C. (Hesse), easily soluble in hot chloroform, soluble in alkalis with a yellow colour.

According to Paternò, by heating with water to 150°, atranorin gives physciol (methyl-phloroglucinol) and atraric acid (betorcinol-carboxylic acid methyl ester), and these substances are also obtained when atranorin is heated with acetic acid in a sealed tube (Hesse).

Physciol forms colourless needles, melting-point 104—105°, gives a blue-green coloration with ferric chloride, and possesses, according to Hesse, the constitution of a methyl-phloroglucinol—

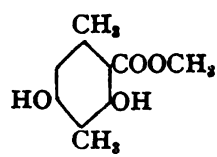


Betorcinol carboxylic acid methyl ester, $C_{10}H_{12}O_4$, crystallises in leaflets, melting-point 140—141° C., and gives a blood-red coloration with calcium hypochlorite solution. Digested with boiling hydroidic acid, it is converted into *β-orcin* (Stenhouse and Groves), $C_8H_{10}O_2$, according to the equation—

$$C_{10}H_{12}O_4 + HI = CH_3I + CO_2 + C_8H_{10}O_2$$

β-orcin (see also *barbatic acid*) is 1 : 4-dimethylresorcin.

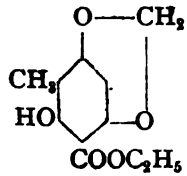
The constitution assigned to betorcinol carboxylic acid methyl ester is—



Heated with alcohol in a sealed tube, atranorin gives, according to Paternò, *hæmatommic acid* and *hæmatomminic acid*; but the researches of Hesse indicate that these compounds in reality consist of *hæmatommic acid methyl ether* and *betorcinol carboxylic acid methyl ether*.

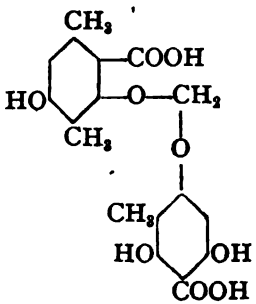
Hæmatommic acid methyl ether, $C_{10}H_{10}O_5$, forms colourless needles, melting-point 147°, soluble in alkaline solutions with a yellow colour. With ferric chloride it gives a purple-red or purple-brown coloration. The *ethyl ether*, $C_{11}H_{12}O_5$, gives colourless needles, melts at 111—

112° (Hesse); 113—114° (Zopf). It is represented by the formula—

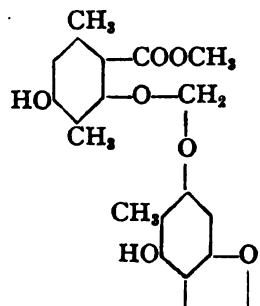


When a solution of atranorin in dilute acetic acid is gently evaporated, *atranorinic acid* (Hesse) is produced. This compound is also present in the *Cladonia rangiformis* (Hesse) when gathered in December, but is absent from the lichen in summer.

Atranorinic acid, $C_{18}H_{18}O_9$, H_2O, forms colourless crystals, which are anhydrous at 100°, and then melt at 157°. With ferric chloride it gives a dark brownish-red coloration. With hydriodic acid it gives *β-orcin*, and when heated with alcohol yields carbon dioxide, *physciol* and *β-orcin*. The constitutions assigned to atranorinic acid (1) and atranorin itself (2) are as follows :—



(1)



(2)

References.—Paternò and Oglialaro (Gazzetta, 7, 289), Paternò (*ibid.*, 10, 157, and 12, 257); Zopf (Annalen, 288, 38); Hesse (J. pr. Chem., 57, 280); Lüdecke (Annalen, 288, 42); Hesse (Annalen, 119, 365); Stenhouse and Groves (Annalen, 203, 302); Hesse (J. pr. Chem., 1906, [ii.], 73, 113).

Barbatic Acid.

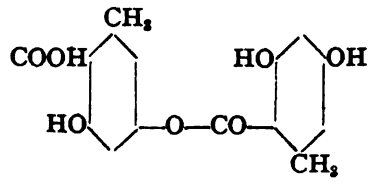
Barbatic acid, $C_{19}H_{20}O_7$, was first isolated from the lichen *Usnea barbata* by Stenhouse and Groves (Chem. Soc. Trans., 1880, 37, 405), in which it occurs in conjunction with usnic acid. Zopf (Annalen,

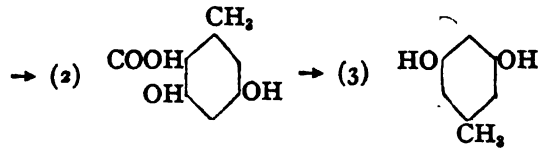
1897, 297, 271) found barbatic acid in the *Usnea longissima*, in the *Electora ochroleuca* (*ibid.*, 1899, 306, 282), and in the *Usnea dasypoga* (*ibid.*, 1902, 324, 39); Hesse (J. pr. Chem., 1898, ii., 57, 232) describes its presence in the *Usnea longissima*, *Usnea barbata*, and *Usnea ceratina*. Hesse (*loc. cit.*) originally considered that barbatic acid had the composition $C_{22}H_{24}O_{8}$ and described potassium barium and copper salts and an ethyl ester, melting-point 132°, which apparently established this formula, but in a later paper (J. pr. Chem., 1903, ii., 68, 1) he adopted Stenhouse and Groves' formula, $C_{19}H_{20}O_{7}$. The *sodium salt*, $C_{19}H_{19}O_{7}Na$, $2H_2O$, crystallises in straight-sided leaflets (compare also Zopf, 1902, 789). The action of acetic anhydride on barbatic acid leads to the formation of a compound which is probably the lactone of acetylbarbatic acid; this melts at 250° and on recrystallisation from acetic anhydride yields *acetylbarbatic acid*, $C_{19}H_{19}(C_2H_3O)O_7$, melting-point 172°. By the hydrolysis of barbatic acid with aqueous alkalis *betorcinol* and *rhizoninic acid* are formed. Barbatic acid crystallises in colourless needles, melting-point 184° (Hesse, J. pr. Chem., 1906, (2), 73, 113).

Archil or Orchil.

Archil or *Orchil* (*Orseille*, Fr.; *Orseille*, Ger.; *Oricello*, It.) appears in commerce in three forms: (1) as a pasty matter called *archil*; (2) as a mass of a drier character, named *persis*; and (3) as a reddish powder called *cudbear*. It is obtained from various lichens of the genus Roccella, growing on the rocky coasts of the Azores, the Canaries and Cape de Verd Isles, also of the Cape of Good Hope, Madeira, Corsica, Sardinia, etc., and from *Ochrolechia tartarea*, growing in Sweden and Norway. None of these lichens contains the colouring matters ready formed, but they contain certain colourless acids of the type of *lecanoric acid*, derivatives of orcin, into which they can be readily converted. Thus, lecanoric acid (1) gives first orsellinic acid (2) and subsequently orcin (3) according to the following scheme (see under Lecanoric Acid):—

(1)





Orcin itself, when acted upon by air and ammonia, changes into a purple substance called *orcein*, which is the name applied to the colouring matters of archil (Robiquet, Ann. Chim. Phys., [2], 47, 238).

Finely powdered orcin is placed in a thin layer under a bell jar, together with a beaker containing strong ammonia solution. As soon as the substance has become brown coloured, it is removed and exposed to air for some time. It is then dissolved in very dilute ammonia solution, reprecipitated with acetic acid, and dried. According to Gerhardt and Laurent, orcein has the composition $C_{14}H_7NO_6$ (Ann. Chim. Phys., [3], 24, 315), but more recent researches indicate that it is a mixture of substances. Liebermann, for instance (Ber., 7, 247; 8, 1649), considers that by this reaction three colouring matters are produced, having respectively the formulæ (*a*) $C_{14}H_{13}NO_4$; (*b*) $C_{14}H_{12}N_2O_3$; and (*c*) $C_{14}H_{12}N_2O_4$.

Zulkowski and Peters (Monatsh., 11, 227) allowed orcin to remain in contact with ammonia for two months, and from the product isolated three substances:—

(*a*) *Red orcein*, $C_{28}H_{24}N_2O_7$, the main product, which appears to be formed according to the following equation:—

$$4C_7H_8O_2 + 2NH_3 + 6O = C_{28}H_{24}N_2O_7 + 7H_2O$$

It is a brown crystalline powder, soluble in alcohol with a red colour, and in alkaline solutions with a blue-violet tint.

(*b*) A crystalline yellow compound, $C_{21}H_{19}NO_5$, which is accounted for as follows:—

$$3C_7H_8O_2 + NH_3 + 3O = C_{21}H_{19}NO_5 + 4H_2O$$

(*c*) An amorphous product similar to litmus.

These substances can be prepared much more rapidly by the addition of hydrogen peroxide to an ammoniacal solution of orcin.

There can be no doubt that this reaction proceeds in several stages, and that the character of the product varies according to the duration of the process. This is well known to manufacturers, who

can prepare at will a blue or a red orchil. The constitution of these colouring matters has not yet been determined, but in view of the circumstances by which they are produced, it is most probable that they are members either of the *oxazine* or *oxazone* groups.

Orchil was originally prepared from the lichens by means of stale urine, which supplied the necessary ammonia, but ammonia solution is now exclusively employed. The older methods have, however, been greatly improved, and in the place of barrels the operation is carried out in large horizontal or vertical cylinders fitted with stirrers, and suitable openings for the admission of air.

In such an apparatus the weed is digested with about three times its weight of ammonia solution at 60° for from three days to one week, the admission of air being regulated according to the judgment of the manufacturer. The first product of the reaction has a blue colour, and if the process be stopped at this point, there is formed the dyeware known as *blue orchil*. On the other hand, if the action of the air and ammonia is allowed to proceed further, *red orchil* is obtained. These orchil pastes when dried and finely ground constitute the product known as *cudbear*.

Bedford (Ger. Pat. 57612, 1889) blows air or oxygen through the ammoniacal mixture, which, especially in the latter case, materially shortens the process. The apparatus employed is erected vertically, and by an ingenious arrangement of projecting shelves, the edges of which are turned down, a considerable quantity of the air or oxygen is entrapped, and exerts therefore a more powerful oxidising effect.

Orchil liquor is prepared by extracting the lichens with boiling water, concentrating the extract to from 8—10° Tw., and submitting this to the action of air and ammonia; whereas *orchil extract* is produced by the extraction of orchil paste itself.

In former times archil and cudbear were frequently adulterated with magenta, certain azocolours, extracts of logwood, brazilwood, etc.; but as the importance of these dyestuffs has now very greatly diminished, such a contamination is at the present time of rare occurrence.

Archil and its preparations are substantive colouring matters, which dye well in a neutral bath, but have the useful property of behaving nearly as well under slightly acid or lightly alkaline conditions. Even colours of considerable intensity are produced from it without difficulty, but unfortunately these are not fast to light. Wool is dyed in a neutral bath, or with addition of a trace of sulphuric acid, and silk is dyed in the presence of soap solution,

acetic acid being sometimes added. Archil is not applied to cotton.

Archil was at one time employed to a large extent for "bottoming" indigo, that is to say, the fabric was first dyed with archil and subsequently with indigo. The reverse process, known as "topping," has again been considerably in vogue. Cudbear and archil are also used to a limited extent in conjunction with other dyestuffs for the production of compound shades. White wines are sometimes coloured with archil, but its presence can be detected by precipitating with lead acetate and extracting with amyl alcohol, when a red colour indicates the presence of archil or magenta. The addition of a little hydrochloric acid changes the colour to yellow if magenta be present, but does not alter it if archil is the adulterant (Haas, Zeitsch. anal. Chem., 20, 869; J. Soc. Chem. Ind., 1, 119).

Litmus.

This colouring matter is well known to the chemist, since white paper impregnated with its solution in a slightly acid or alkaline condition has long been employed, under the name of red and blue litmus-paper, to indicate the presence, in any solution, of alkalis or acids respectively. Alkalis change the colour of red litmus-paper to blue, acids turn blue litmus-paper red. In alkalimetry litmus tincture has, until recently, been the most generally adopted indicator. This use depends upon the fact that the free colouring matter of litmus is red, whereas its alkali salts are blue.

Commercial litmus has the form of small pale blue cubes, composed essentially of gypsum and chalk mixed with but comparatively little colouring matter, which is largely present in the form of a lake.

It is said to be prepared, chiefly in Holland, from various species of lichens, e.g. *Lecanora tartarea*, *Roccella tinctoria*, etc., the same, indeed, as are used in the manufacture of orchil (q.v.). Under the combined influence of ammonia and atmospheric oxygen the proximate principles contained in these lichens yield *orcein*, the alkali salts of which are purple (orchil); but if potassium or sodium carbonate is present at the same time, the reaction proceeds further, and ultimately *azolitmin* (the colouring matter of litmus), the alkali salts of which are blue, is produced.

According to Gélis (J. Pharm. Chim., 24, 277; Revue Scient., 6, 50), litmus may be prepared as follows. Orchil-weed is ground and mixed with half its weight of potassium carbonate, and then repeatedly moistened with urine saturated with ammonium carbonate or with an aqueous solution of this salt; the mass soon acquires a

brownish-red colour (three days), which gradually becomes purple (twenty to twenty-five days), and finally blue (thirty days), yielding a litmus of the best quality in forty days. The pulpy mass is mixed with chalk and gypsum, then moulded in the form of cubes, and dried.

By modifying the action of air and ammonia upon orcinol, through the addition of sodium carbonate, De Luynes also succeeded in obtaining the colouring matter of litmus (Comptes rend., 59, 49; Dingl. poly. J., 174, 61; Chem. Zentr., 1865, 127; J., 1864, 551). A mixture of 1 part orcinol, 25 parts crystallised sodium carbonate, 5 parts water, and 5 parts ammonia solution, was heated to 60—80° for four to five days with frequent agitation. On diluting the blue solution thus obtained and acidifying slightly with hydrochloric acid, the colouring matter was precipitated. On washing and drying, it assumed a metallic lustre. It is sparingly soluble in water, but readily soluble in alcohol and in ether.

In making a litmus solution to be employed as indicator, the commercial litmus is extracted with boiling water, the filtered solution is slightly acidified with acetic acid, then carefully neutralised with ammonia, and boiled to expel any excess of the latter. Kept for any lengthened period in stoppered bottles, the solution becomes decolorised in consequence of a reductive fermentation; on exposure to air, however, the original colour is restored. This defect is prevented by saturating the solution with sodium chloride (Reichelt), (compare also Bellamy, J. Pharm. Chim., [v.], 18, 433). A dry litmus-extract may be prepared, according to Vogel, in the following manner (*ibid.*, 45, 64, 70; Chem. News, 1864, 205). Twenty grams powdered commercial litmus are twice digested, each time with 150 c.c. cold distilled water. The second solution, which is alone employed, is divided into two equal portions, one of which is slightly acidified with nitric acid and then mixed with the other. The purplish solution thus obtained is evaporated to dryness on the water-bath, and the granular amorphous mass is kept in a stoppered bottle ready for dissolving in water when required.

For the employment and characteristics of litmus as an indicator, *v.* R. T. Thomson (J. Soc. Chem. Ind., 6, 198); also art. ACIDIMETRY, vol. i.; Marsh (Chem. News, 61, 2); Berthelot (Ann. Chim. Phys., [vii.], 25, 39); Ronde (Pharm. Zeit., 41, 736); Lescouer (Comptes rend., 123, 811); Lüttke (Zeitsch. anal. Chem., 31, 692); Foerster (*ibid.*, 28, 428); Glaser (*ibid.*, 38, 273).

Litmus exhibits a characteristic absorption spectrum. Ether extracts it from an acid solution, and forms a yellow liquid, which

absorbs the more refrangible end of the spectrum to a point midway between D and E. If the solution is coloured blue by adding a drop of ammonia, an absorption-band is formed, commencing at D, where it is extremely black, and gradually diminishing to E. A blue aqueous commercial solution shows a well-marked absorption-band at D. Addition of acid changes the colour to red, the band at D disappears, and the spectrum now resembles that of œnolin, the colouring matter of red wine (A. H. Allen, Com. Org. Analysis, 325), (compare also Vogel, Praktische Spectralanalyse, 1877, 269).

Our knowledge of the chemistry of the colouring matters contained in litmus is very meagre. Gélis (J. Pharm. Chim., 27, 477) isolated from it several compounds in the following manner. After extracting commercial litmus with water, the insoluble residue is boiled with dilute caustic alkali and the filtered solution is precipitated with basic lead acetate. The blue precipitate is washed by decantation until it begins to dissolve and colour the wash-water. It is then decomposed with hydrogen sulphide, exposed to air until free from excess of H_2S, collected on a filter and digested with dilute ammonia to extract the colouring matter. On adding acid to the filtered solution the main portion of the litmus colouring matters is thrown down as a red flocculent precipitate. The filtrate from this contains a very small quantity of substance (α).

On extracting the dried red precipitate with ether and leaving the orange solution to spontaneous evaporation, it yields a bright red residue (β) containing crystalline needles. This product is insoluble in water, but readily soluble in alcohol, also in alkalis with a violet colour. The portion insoluble in ether is dissolved in alcohol, and on allowing the blood-red solution to evaporate spontaneously it yields a large quantity of a reddish-purple product (γ) having a bronze lustre. This represents the colouring matter most abundant in litmus.

The residue, which is insoluble in water, in alcohol, and in ether, contains another product (δ) which is soluble in alkalis, from which it may be precipitated by acids. The three products β, γ, and δ, appear to contain nitrogen.

An examination of litmus was made in 1840 by Kane (Royal Soc. Trans., 1840, 298; Ann. Chim. Phys., [iii.], 2, 129; Annalen, 39, 57; J. Pharm. Chim., 1841, 569), who isolated from it the chief and characteristic colouring matters *azolitmin* and *erythrolitmin*, together with *erythrolëin* and *spaniolitmin*.

According to Kane, finely powdered commercial litmus is extracted with boiling water. Most of the colouring matter remains

in the form of an insoluble lake in the residue, to which hydrochloric acid is added till effervescence ceases and the mixture is strongly acid. The insoluble matter interspersed with liberated colouring matter is collected on a filter, washed free from acid, dried, and extracted with boiling alcohol. The alcoholic solution is filtered from an insoluble reddish-brown mass (impure azolitmin) and then evaporated to dryness, and the residue is digested with warm ether until it becomes no longer coloured. On distilling the filtered ethereal solution, *erythroleïn* is left as a purple semi-fluid oily substance. That portion of the alcoholic extract which is insoluble in ether consists of *erythrolitmin*.

The above-mentioned impure azolitmin is purified, either by dissolving it in a large quantity of boiling water and evaporating the solution to dryness, or by dissolving it in very dilute ammonia, evaporating the solution to dryness, neutralising any residual ammonia by dilute hydrochloric acid, and washing with alcohol until free from ammonium chloride and excess of hydrochloric acid. The residue represents purified *azolitmin*.

The colouring matter contained in the deeply coloured solution obtained in the first instance by boiling the commercial litmus with water and filtering, is isolated as follows. The solution is precipitated with neutral lead acetate, the purple precipitate thus obtained is well washed, suspended in water, and decomposed with hydrogen sulphide. The mixture of lead sulphide and liberated colouring matter thus obtained is well washed and digested with warm dilute ammonia; the filtered deep-blue solution is evaporated to dryness, the residue is moistened with hydrochloric acid, washed free from ammonium chloride and any excess of hydrochloric acid, with warm alcohol. The residual deep brownish-red powder consists usually of nearly pure azolitmin, more rarely of *spaniolitmin*, a substance very similar to azolitmin, but which does not contain nitrogen.

Since spaniolitmin occurs so rarely in litmus, and erythroleïn is coloured reddish-purple and not blue by alkalis, Kane considers azolitmin and erythrolitmin to be the essential colouring matters of litmus, in which they are combined with ammonia, potash, and lime, and mixed with a considerable quantity of chalk, gypsum, etc.

Azolitmin is a deep brownish-red amorphous powder, insoluble in alcohol and sparingly soluble in water, but readily soluble in alkaline solutions with a pure blue colour. Its ammoniacal solution gives with metallic salt solutions blue or purple precipitates according as they are more or less basic in character. Kane's formula for azolitmin is $C_9H_{10}NO_5$, but Gerhardt considers it is best represented

by $C_7H_7NO_4$. It differs from all the other colouring matters isolated from litmus by containing nitrogen. Gerhardt considered it to be derived from orcinol, possibly in accordance with the following equation:—

$$C_7H_6O_2 + NH_3 + 3O = C_7H_7NO_4 + H_2O,$$

or from orceïn thus, $C_7H_7NO_3 + O = C_7H_7NO_4$.

If the percentage composition assigned to this substance is correct, the explanation of the part played by the necessary alkaline carbonate in the manufacture of litmus may be that it facilitates and increases the oxidation of the orcinol, so that the orceïn at first formed is changed into azolitmin (Gerhardt, Ch. Org., 3, 816).

Scheitz (Zeitsch. anal. Chem., 1910, 49, 736) has isolated from litmus a blue colouring matter distinct from azolitmin in quantity equivalent to 1·5 per cent. of the weight of the purified material. It consists of a bright brown powder soluble in formic acid, pyridine, and ammonia, forming a bluish-violet solution with the last-named solvent. It absorbs ammonia gas with production of a dark blue ammonia compound, which dissolves in water to a reddish solution. This ammonia compound is a more delicate indicator than the corresponding derivative of azolitmin.

Erythrolitmin, which also constitutes one of the most important ingredients of litmus, is a bright-red powder, sparingly soluble in water and in ether. It is abundantly soluble in alcohol, from which it may be crystallised in the form of dark-red granular crystals. In strong caustic potash it dissolves with a blue colour. With ammonia it forms a blue compound which curiously enough is totally insoluble in water. With metallic salts it forms lakes of a fine purple colour. According to Kane its formula is $C_{13}H_{22}O_6$, and he considers it to be an oxidation product of his erythroleïc acid ($C_{13}H_{22}O_4$) obtained from orchil.

Erythroleïn forms a crimson semi-fluid mass, almost insoluble in water, soluble in ether and in alcohol with a red colour, and in ammonia with a purple colour. With metallic salts it gives purple lakes. Kane gives its formula as $C_{13}H_{22}O_2$. Its general properties are very similar to those of the above-mentioned erythroleïc acid.

Spaniolitmin occurs but rarely in litmus, hence its name. It is a bright-red substance, insoluble in alcohol and in ether, and very sparingly soluble in water. It dissolves in alkalis with a blue colour and gives lakes very similar to those of azolitmin. Kane's formula for it is $C_9H_7O_8$.

Under the influence of hydrogen sulphide, the colouring matters

of litmus are decolorised, Kane's idea being, that a colourless hydrogen sulphide compound is thus formed (*v.* also Malaguti, Ann. Chim. Phys., (iii.), 37, 206; Vogel, J. pr. Chem., (ii.), 16, 311). Nascent hydrogen, and other reducing agents such as ferrous and stannous oxide, etc., also decolorise them by reduction in the ordinary manner. Azolitmin thus yields colourless *leucazolitmin*, which, however, rapidly oxidises and becomes coloured on exposure to air. If stannous chloride is added to an ammoniacal solution of azolitmin, purple-coloured stannous-azolitmin is precipitated; if this is boiled with slightly acidulated water there is formed the colourless compound of stannic oxide with leucazolitmin, which, if exposed to air, changes into the bright scarlet stannic-azolitmin.

Deoxidising agents such as sulphurous acid and sulphites do not decolorise the colouring matters of litmus.

Azolitmin and erythrolitmin, suspended in water and submitted to the action of chlorine gas, are decolorised and give yellow chlorine derivatives, *chlorazolitmin* and *chlorerythrolitmin*, substances insoluble in water, but soluble in alcohol, ether, and in alkalis.

In his earliest memoir, Kane (Annalen, 36, 324) mentions that on heating the colouring matters of litmus mixed with chalk or gypsum, a red vapour is given off which condenses in the form of crystalline scales (atmérythrin) soluble in alcohol. When heated alone, this substance is not produced. Although Kane makes no subsequent mention of this body it is possible that it was indirubin or even indigotin, since at a later date Wartha (Ber., 9, 217) states that he found some samples of litmus to contain indigotin, recognisable by the violet vapour given off on heating a few cubes of the commercial product in a test tube. Its presence may have been due to the use of urine containing indoxyl in the preparation of the litmus.

Wartha (*loc. cit.*) gives the following results of his examination of litmus. The commercial product is well shaken up with alcohol; the filtered purple solution thus obtained has a green fluorescence, and exhibits in the spectroscope a characteristic absorption band in the green with an almost total absorption of the violet end. The colouring matter (*a*) itself is obtained on evaporating the solution.

The litmus residue insoluble in alcohol is digested for twenty-four hours with distilled water, and the filtered deep-coloured solution is evaporated to dryness. The extract thus obtained is repeatedly treated with absolute alcohol containing a little glacial acetic acid and again evaporated, so that all traces of water may be removed, and there finally remains a brown powdery mass. On extracting this

with absolute alcohol, a large quantity of a scarlet substance (*b*) is dissolved. It is similar to orceïn and dissolves in ammonia with a reddish-purple colour. That portion of the brown powder which is insoluble in the acidified alcohol is dissolved in water, the filtered solution is evaporated to dryness, and the residue is repeatedly washed with absolute alcohol and evaporated in order to expel all traces of acetic acid. The residual brown powder, which is very soluble in water, with a reddish-brown colour, but insoluble in alcohol and in ether, is the purified and extremely sensitive colouring matter of litmus (*c*). Its alkaline solution is blue, its aluminium and tin lakes are violet, and its calcium and barium lakes blue. It appears to be very similar to Kane's azolitmin, but it is said not to contain nitrogen. The yield of these various colouring matters is as follows: (*a*) 2·3 per cent., (*b*) 3·4 per cent., (*c*) 5·7 per cent. (Mitchell, Chem. News, 1876, 140).

An examination of the colouring matters of litmus was also made by Rochleder and Skraup (Wien. Anz., 1874, 118; Chem. Zentr., 1874, 424). Other references are Magner, J. Pharm. Chem., 12, 418; Desfosses, *ibid.*, 14, 487; Peretti, *ibid.*, 14, 539.

Of interest also in connection with this subject is the fact that when ethyl-amino-orsellinic acid is oxidised by air in alkaline solution it yields an orange-coloured dye possessing basic properties (Heinrich and Dorschky, Ber., 1904, 37, 1416).

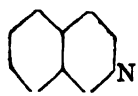
A peculiar blue colouring matter similar to litmus, and called *tournesol en drapeaux*, has long been manufactured at Grand-Gallargues, Département du Gard, France, from the *Croton tinctorium* belonging to the *Euphorbiaceæ*. Coarse linen cloth is steeped in the deep bluish-green sap expressed from the berries and the tops of the plant, then dried quickly in the open air, and exposed for one to one and a half hours between layers of straw to the ammoniacal vapours of lant or horse-dung (*aluminadon*), care being taken not to submit them to this influence too long. The cloth thus acquires a deep blue colour. It is then steeped in the sap a second time and dried in air till it acquires a purple or dull green. These blue cloths are or were used by the Dutch farmers for making an infusion with which to impart a red colour to the outside of their cheese, the blue being changed to red by the lactic and butyric acids of the cheese.

According to Joly (Ann. Chim. Phys., [iii.], 6, 111) the colouring matter pervades the entire plant and is readily extracted therefrom by water heated to 50—60°. On being evaporated, an azure-blue resinous mass remains. Acids change the blue colour of its aqueous

solution red, and this blue is not restored by alkalis, the colour becoming thereby rather greenish. It is, therefore, probably quite distinct from the colouring matter of litmus, and is, indeed, more similar to the blue colouring matter which can be extracted from another plant belonging to the *Euphorbiaceæ*, viz. *Mercurialis perennis*.

CHAPTER XVII.

ISO-QUINOLINE GROUP.



Barberry—*Evodia meliaefolia*—*Toddalia aculeata*.

BARBERRY.

BARBERRY or berberry, *Berberis vulgaris*, is a compact bush which attains to a height of from 8—10 feet, and is found wild in Great Britain and throughout most parts of Europe and North America. The colouring matter present is *berberine*, and this, though occurring mainly in the bark, is also present in the stem and root of the plant.

Until recently a concentrated commercial extract of this material, known as "Barberry extract," was to be found on the market, and employed for dyeing silk and leather. It does not appear to have been at any time extensively used for these purposes, and is now apparently obsolete.

Barberry is, however, interesting, in that it contains the only natural basic dyestuff at present known, and may, in fact, be applied to fabrics in the same way as the artificial basic colouring matters. Silk and wool, for instance, may be dyed yellow by means of a faintly acidulated decoction of the material, preferably at from 50—60°, whereas for cotton, a tannin antimony mordant is necessary.

For the isolation of berberine the procedure is simple, and consists merely in extracting the ground dyestuff with boiling water containing a slight excess of lead acetate. The concentrated extract is mixed with hydrochloric acid when, on cooling, crystals of berberine hydrochloride separate. Berberine hydrochloride, $C_{20}H_{18}O_4NCl$,*

* The substance commonly known as *berberine hydrochloride* is, in fact, not a hydrochloride, but a quaternary chloride containing the grouping given below,

when pure, crystallises in long silky needles which possess an intense yellow colour and are soluble in hot water and alcohol. The most reliable of the earlier analyses of berberine are those given by Perrins (Annalen, Supp., 2, 176), who suggested the formula $C_{20}H_{17}NO_4$, but it is now known that berberine has the composition $C_{20}H_{19}NO_5$. The base berberine (or berberinal) is best obtained by adding strong caustic soda to the aqueous solution of the sulphate and extracting the product with ether, from which it separates in yellow needles and melts at 144° (Gadamer, Archiv der Pharm., 1905, 243, 34). Berberine is a strong base, yielding well-defined crystalline salts of a deep yellow colour, of which the following may be given as examples:—

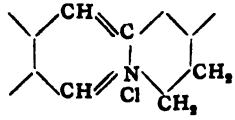
Berberine nitrate, $C_{20}H_{18}NO_4 . NO_3$, *Berberine hydrochloride*, $C_{20}H_{18}NO_4Cl$, *Berberine hydriodide*, $C_{20}H_{18}NO_4I$, and *Berberine platinichloride* $(C_{20}H_{18}NO_4)_2PtCl_6$.

The most important of the early work on berberine is that of Hlasiwetz and Gilm (Jahres., 1864, 407), who by reducing the base with zinc and sulphuric acid prepared *tetrahydroberberine*, $C_{20}H_{21}NO_4$, and by fusion with alkali obtained the acids $C_9H_8O_5$ and $C_8H_8O_5$, the second of which was termed *berberinic acid*. Perkin (Chem. Soc. Trans., 1889, 55, 89), who subsequently examined this latter compound and found that its properties agreed in all respects with those given by Hlasiwetz and Gilm, has shown that it possesses the constitution of a *homocatechol carboxylic acid*.

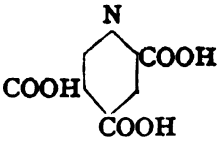
Interesting is also the fact that by the alkali fusion of berberine, or by distilling it with lime, Bernheimer and Bödecker isolated an oily base which they regarded as quinoline, but which is now known to be *iso-quinoline*.

The most valuable results, however, have been afforded by a study of the oxidation products of berberine hydrochloride. Weidel, who employed nitric acid for this purpose, obtained *berberonic acid*, $C_8H_5NO_6$, which he rightly regarded as a pyridine tricarboxylic acid, and this has been more recently shown to consist of the 2 : 4 : 5 compound—

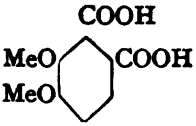
and should be named *berberinium chloride* (W. H. Perkin, Chem. Soc. Trans., 1918, 113, 503)—



The old names for this and the other salts described are, however, retained in this article.



whereas Schmid and Schilbach (Arch. Pharm., [3], 25, 164) by the action of permanganate obtained some quantity of *hemipinic acid*—



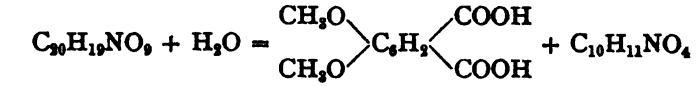
Subsequently, W. H. Perkin, junr. (Chem. Soc. Trans., 1889, 55, 75; 1890, 57, 991; 1910, 97, 323) published a series of elaborate researches on this subject, and it is almost entirely to these that our present knowledge of berberine is due. By adopting special precautions and by the employment of a very large quantity of material, this author succeeded in obtaining from berberine hydrochloride by the action of permanganate, numerous important compounds, the study of which gave the clue to its constitution. The operations employed are of too involved a nature to be dealt with in detail here, but a general idea of the methods employed can be gathered from the following scheme (p. 570) drawn up by the investigator himself (*loc. cit.*, 1890).

Among the oxidation products of berberine, anhydroberberilic acid and berberal have proved to be the most important, and these only will be discussed here in detail.

Anhydroberberilic acid, $C_{20}H_{17}NO_8$, as its name denotes, is an anhydro derivative of berberilic acid, into the sodium salt of which it is readily transformed by the gentle action of sodium hydroxide solution—

$$C_{20}H_{17}NO_8 + 2NaOH = C_{20}H_{17}NO_9Na_2 + H_2O$$

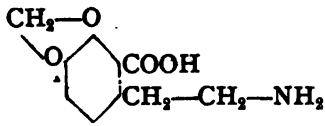
Berberilic acid, $C_{20}H_{19}NO_9$, though only slowly attacked by alkalis, is readily hydrolysed by boiling dilute sulphuric acid, and Perkin thus obtained hemipinic acid and a basic compound, $C_{10}H_{11}NO_4$—



This latter substance proved to consist of *ω-aminoethylpiperonyl carboxylic acid*—

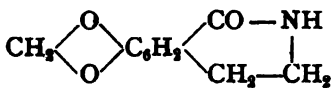
BERBERINE HYDROCHLORIDE IS OXIDISED WITH POTASSIUM PERMANGANATE, THE PRODUCT TREATED WITH SULPHUROUS ANHYDRIDE AND FILTERED.

<table>
<tr><td colspan="4">Yellow Precipitate Treated with Warm Dilute Sodium Carbonate Solution and Filtered.</td><td colspan="5">Yellow Filtrate Evaporated to Half its Bulk and Filtered.</td></tr>
<tr><td colspan="3">Residue boiled with acetic acid and filtered hot.</td><td rowspan="2">Solution contains berberilic acid, $C_{20}H_{19}NO_9$, and some anhydroberberilic acid, $C_{20}H_{17}NO_8$.</td><td rowspan="2">Precipitate contains oxyberberine, $C_{20}H_{17}NO_5$, dioxyberberine, $C_{20}H_{17}NO_6$, anhydroberberilic acid, $C_{20}H_{17}NO_8$.</td><td colspan="4">Solution evaporated to half its bulk and extracted twenty times with ether.</td></tr>
<tr><td rowspan="2">Residue contains berberine hydrogen sulphite, $C_{20}H_{17}NO_4, H_2SO_3$.</td><td colspan="2">Solution on cooling deposits crystals which are separated by filtration.</td><td colspan="4">Ethereal solution evaporated, residue boiled with dilute sodium carbonate solution and filtered hot.</td><td rowspan="2">Aqueous solution contains hemipinic acid, $C_{10}H_{10}O_6$, ω-amidoethylpiperonylcarboxylic anhydride, $C_{10}H_9NO_5$, and inorganic salts.</td></tr>
<tr><td>Residue consists of anhydroberberilic acid, $C_{20}H_{17}NO_8$.</td><td>Solution contains berberal, $C_{20}H_{17}NO_7$.</td><td>Residue contains hemipinic anhydride, $C_{10}H_8O_5$.</td><td colspan="3">Solution allowed to cool and filter.</td></tr>
<tr><td colspan="5"></td><td>Crystals of ω-amidoethylpiperonylcarboxylic anhydride, $C_{10}H_9NO_5$.</td><td colspan="2">Solution acidified with hydrochloric acid and filtered.</td></tr>
<tr><td colspan="5"></td><td>Residue contains berilic acid, $C_{20}H_{18}NO_8$.</td><td>Solution contains hydrastic acid, $C_9H_6O_5$, and hemipinic acid, $C_{10}H_{10}O_6$.</td></tr>
</table>

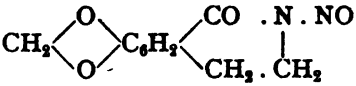


and the main facts which lead to the determination of its constitution are as follows :—

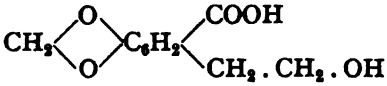
When boiled with water, it readily loses the elements of water with production of the anhydride—



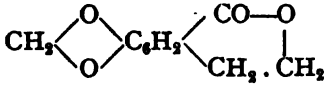
which reacts with nitrous acid to give the nitroso derivative—



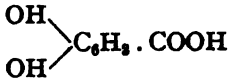
and this compound with dilute caustic soda evolves nitrogen with the production of *ω-hydroxyethylpiperonyl carboxylic acid*—



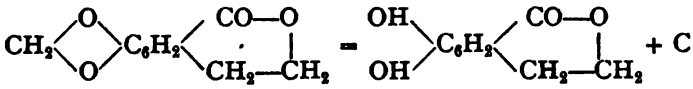
The anhydride—



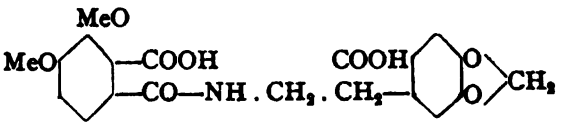
readily obtained from this latter by merely boiling with water, when fused with alkali yields *catechol* and *protocatechuic acid*—

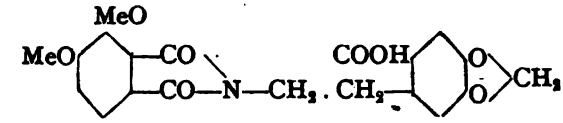


and by the action of hydrochloric acid at 170—175° is converted with loss of carbon, a reaction characteristic of piperonal derivatives, into *hydroxyethylcatecholcarboxylic anhydride*—

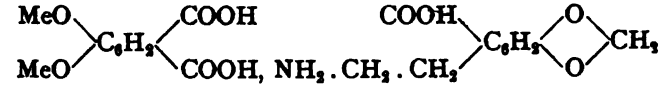


As the result of these experiments, there could be little doubt that berberilic acid (1) and its anhydride (2) possess the constitutions given below—

(1) 

(2) 

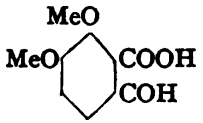
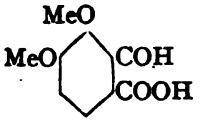
and that these are correct was subsequently established by the observation that the hemipinate of ω-aminoethylpiperonylcarboxylic acid (3) on heating is transformed into anhydroberberilic acid—

(3) 

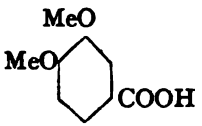
BERBERAL.

As in the case of berberilic acid, the constitution of berberal has been established mainly by a study of the products of its hydrolysis. By the action of alcoholic potash it yields the ω-aminoethylpiperonylcarboxylic acid discussed above, and an acid $C_{10}H_{10}O_5$, and thus resembles berberilic acid which under similar conditions gives hemipinic acid in the place of this latter.

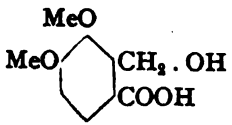
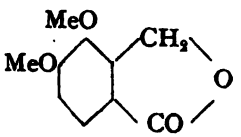
The acid $C_{10}H_{10}O_5$ on examination proved to be constituted similarly to opianic acid (1), and was, therefore, termed *pseudo-opianic acid* (2)—

(1)  (2) 

Thus by the action of caustic potash solution it gave veratric acid—



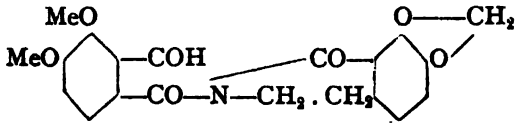
and when reduced formed the unstable acid (3) which readily passed into *pseudomeconine*—

(3)  (4) 

Perkin now found that whereas pseudo-opianic acid and ω-amino-ethylpiperonylcarboxylic acid on heating together give first the salt of the base, that this subsequently by elimination of water passes into berberal—

$$C_{10}H_{10}O_5 + C_{10}H_9NO_3 = C_{20}H_{17}NO_7 + H_2O$$

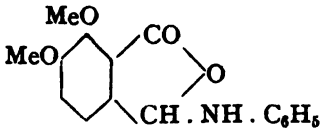
Apparently, therefore, berberal could be represented as follows:—



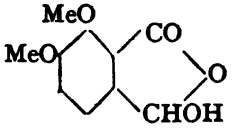
and this formula was at first adopted.

Liebermann, however (Ber., 1896, 29, 175), subsequently pointed out that when opianic acid reacts with aniline to form anilinoopianic acid (1) the latter behaves as a derivative of hydroxyphthalide (2)—

(1)

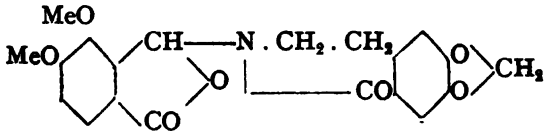


(2)

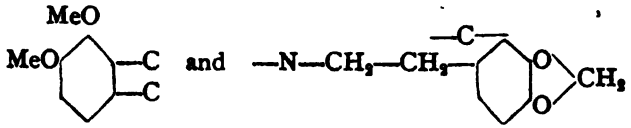


and it is now generally accepted that in the condensations of opianic acid with basic substances, it is always the carbon atom of the aldehyde group which becomes attached to the nitrogen in the final product.

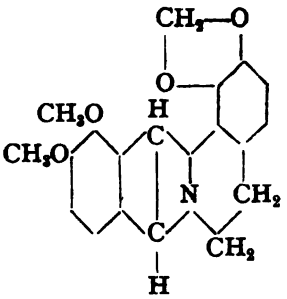
As a result of this later work, Perkin and Robinson (*loc. cit.*) have modified the original expression for berberal as follows:—



An examination of the formulæ both of berberilic acid and of berberal, led Perkin in 1890 to the consideration that in berberine the following groups of atoms are present—



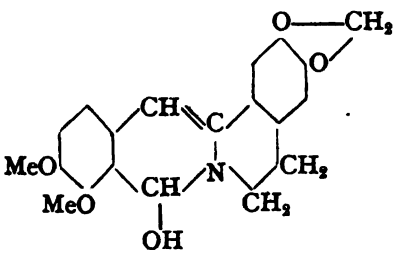
and that, in order to construct a formula for this alkaloid, these require to be united with the addition of but one atom of hydrogen. As a result the following constitution was assigned to this alkaloid—



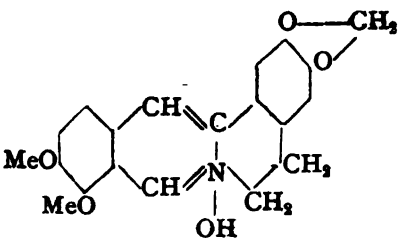
this structure being based upon the older formula of berberine, $C_{20}H_{17}NO_4$, which at that time was considered to be correct.

Recently Perkin and Robinson (*loc. cit.*, p. 318) have pointed out that the methylenedioxy-group in Perkin's original formula had been incorrectly placed, as was evident from an examination of the structure of ω-aminoethylpiperonylcarboxylic acid (cf. also Freund and Beck, Ber., 1904, 37, 4673). Moreover, as a result of the newer views of the former authors as to the constitution of berberal (*loc. cit.*) the position of the methoxy groups in the old berberine formula required modification. It is now considered that berberine has the formula $C_{20}H_{19}O_5N$, and is represented by formula (1), and that for the purpose of salt formation it undergoes change into the modification called berberinium hydroxide (2), from which the salts are obtained by the replacement of the OH group by the acid radicle—

(1)

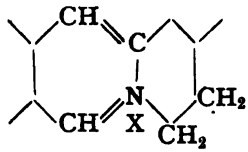


(2)



The reasons for this assumption (W. H. Perkin, jun., Chem. Soc. Trans., 1918, 113, 503) are based on the similarity between berberine and cotarnine, but are too complex to enter into in this article, and for their understanding the literature must be consulted (cf. Robinson and Robinson, Trans., 1917, 111, 958).

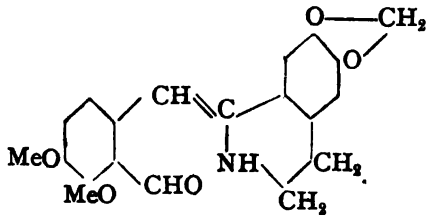
Interesting is the fact that though the salts of berberine are derived from the hydroxyl formula and contain the grouping—



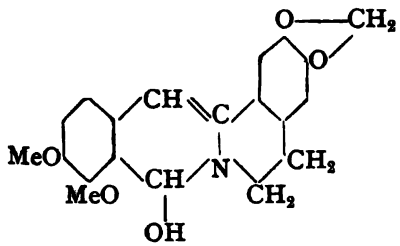
(where X = Cl, HSO_4, NO_3, etc.), the alkaloid itself exists as a different modification.

When berberine sulphate is treated with barium hydroxide (Gadamer), a strongly alkaline liquid is produced which possibly contains the hydroxy modification of berberine (berberinium hydroxide), but if to this solution excess of sodium hydroxide is added, the yellow modification known as *berberinal* is obtained. The constitution assigned to this substance by Gadamer was—

(1)



but its most probable structure is that represented by the formula—

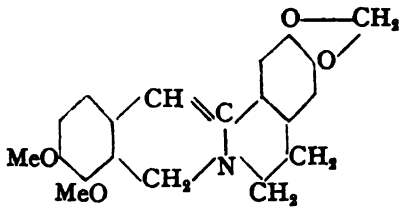


(compare Tinkler, Chem. Soc. Trans., 1911, 99, 1345).

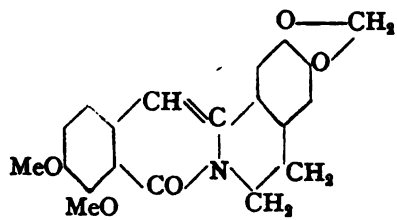
When treated with excess of alkali, berberinal yields dihydroberberine (1) with simultaneous formation of oxyberberine (2), owing, according to Gadamer, to the conversion of the COH

group into $CH_2(OH)$ and COOH in the manner characteristic of aromatic aldehydes—

(1)



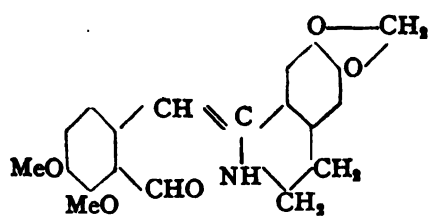
(2)



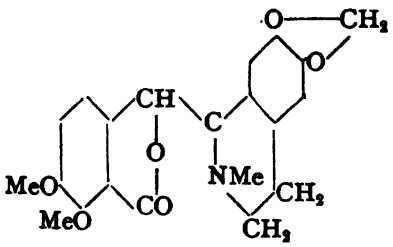
The latter compound as indicated in the table on p. 570 was first obtained by Perkin as an oxidation product of berberine.

On the other hand, Faltis (Monatsh., 1910, 31, 557) considers the reaction of berberinal with alkali to be similar to that which takes place between quinoline methiodide under the same conditions and that the products of the reaction are oxyberberine and tetrahydroberberine (cf. Decker, 1903, 1205 and 2568). It has, however, recently been shown conclusively that Faltis' view is incorrect (W. H. Perkin, private communication).

Berberine is closely allied to hydrastine, which occurs along with it in *hydrastis canadensis*, and the relationship between these compounds is clearly evident, if the formula of Gadamer for berberinal and that of hydrastine (see above) are compared—



Berberinal.



Hydrastine.

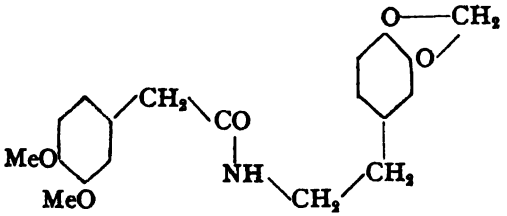
In 1911 Pictet and Gams (Ber., 1911, 44, 2480) were successful in effecting the synthesis of berberine by the following series of reactions.

Homopiperonylamine, $CH_2 : O_2 : C_6H_3 . CH_2 . CH_2 . NH_2$, by condensation with the chloride of homoveratric acid,

$$(CH_3O)_2C_6H_3 . CH_2 . COCl,$$

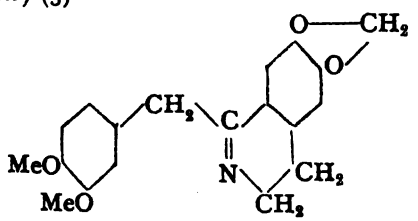
yields *homo-veratroyl-homopiperonylamine* (1)—

(1)

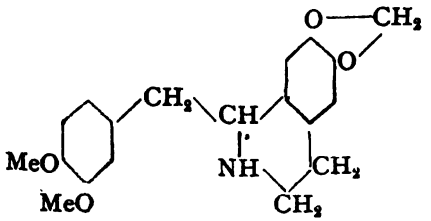


and this compound on treatment with phosphorus pentoxide in the presence of boiling xylene is transformed into the dihydro-quinoline base (2). By reduction with tin and hydrochloric acid this passes into *veratroyl-methylene-dioxy-tetrahydro-iso-quinoline* (*veratryl nor-hydro-hydrastinine*) (3)—

(2)

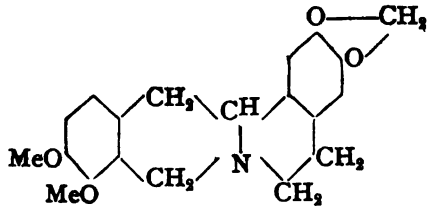


(3)

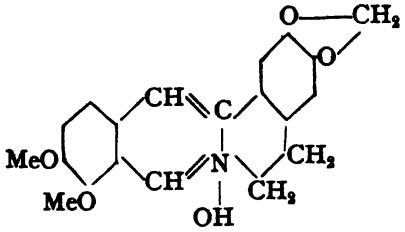


which on treatment with methylal, $CH_2(OCH_3)_2$, gives *tetrahydroberberine* (4), a compound originally prepared by Hlasiwetz and Gilm, and subsequently examined by Perkin and others. This by the action of mild oxidising agents such as iodine or mercuric acetate is readily transformed into berberine (5)—

(4)



(5)



For the synthesis of oxyberberine the paper of Pictet and Spengler (Ber., 1911, 44, 2036) must be consulted.

Numerous plants contain berberine, and though most of these have been or are used medicinally, their employment for dyeing has apparently been of rare occurrence. The following list embodies most of these:—

Berberis aquifolium (Gordin, Arch. Pharm., 1902, 240, 146), *B. oetnensis* (Perkin, Chem. Soc. Trans., 1897, 71, 1198), *Cossinium fenestratum* and *Xanthorrisa aquifolia* (Perrins, Annalen, 83, 276), *Hydrastis canadensis* (Mahla, Amer. Chem. J., [2], 33, 843), *Coptis aceta* and *C. trifolia*, *Chelidonium majus* and *Stylophorum diphyllum* (Schlotterbeck, Amer. J. Pharm., 1902, 74, 584), *Evodia meliæfolia* and *Toddalia aculeata* (Perkin and Hummel, Chem. Soc. Trans., 67, 414), *Xanthoxylum clava Herculis* (Chevallier and Pelletan, Journ. de Chim. Médicale, 1826, 2, 314), yellow Assam wood or "Woodumpar" (Crookes' "Dyeing and Calico Printing"), *Coeloeline polycarpa* (Stenhouse, Annalen, 66, 384; 69, 40), *Archangelisa lemnis-cata* (Becc.) and *Mahonia nepalensis* (D.C.), (Brooks' Philippine Journ. of Science, 1910, v., 442).

For the commercial preparation of berberine the *Hydrastis canadensis*, which contains about 4 per cent. of the alkaloid, forms the best available material.

EVODIA MELIAEFOLIA.

This tree, belonging to the *Rutaceæ*, is found in China and Japan, where its bark is largely employed in dyeing and in medicine. It was formerly described by Loureiro as *Ptero-carpus flavus*, but this error was eventually corrected by P. W. Squire (Pharm. J., (3), 1888, 18, 785), who showed it to be really *Evodia glauca*, which is synonymous with *E. meliaefolia*. By qualitative tests, Martin, Tokio (Arch. Pharm., 1878, 13, 337) and Squire (*loc. cit.*) suspected the presence of *berberine*, and this colouring matter was subsequently isolated by Perkin and Hummel (Chem. Soc. Trans., 67, 415).

TODDALIA ACULEATA.

Toddalia aculeata (Pers.).—This Indian plant, belonging to the *rutaceæ*, is a rambling shrub found in the sub-tropical Himalayas, in the Khasia mountains, and throughout the Western Peninsula and Ceylon.

The root bark is or was used in Madras as a yellow dyestuff, and it is also highly spoken of by various writers as one of the most valuable Indian medical products, possessing tonic, stimulant, and antipyretic properties. It was introduced into European medicine in 1771, and at one time enjoyed some celebrity under the name of "Lopez Root," but it has long since fallen into disuse. According to Brooks (Philippine Journal of Science, 1910, v., 442) this plant is common in the Philippines, but so far as is known is not used as a dye by the natives. The colouring matter it contains is *berberine* (Perkin and Hummel, Chem. Soc. Trans., 67, 413).

CHAPTER XVIII.

COLOURING MATTERS OF UNKNOWN CONSTITUTION.

Insoluble Red Woods: Sanderswood—Barwood—Caliaturwood—Narrawood—Camwood—Red Dura—Safflower—Species of *Coprosma*—Kamala—Waras—Saffron—Green Ebony—Cotton Seed—*Eriococcus coriaceus*—Annatto—*Nycanthes arbor-tristis*—*Cedrela toona*—Algarrobin—*Lycoperdon gemmatum*—Phoenin and Phoenicein—Lokao.

The Insoluble Red Woods.

The dyestuffs of this small group, Sanderswood, Barwood, Caliaturwood, Camwood, and Narrawood, all possess very similar dyeing properties, and owing to the sparing solubility in water of the resinous colouring matters which they contain, they are called "insoluble red" woods. They cannot, therefore, be made to yield the same type of commercial extract as is given by the soluble red woods, Brazilwood, Sapanwood, etc.

These dyewoods are chemically interesting in that the colouring matter present is substantive to wool, and thus, by merely boiling the material in an aqueous extract of the wood, or in a bath containing this in suspension, a brick-red shade is produced. It is remarkable, however, that though the tinctorial constituents of all these woods are readily soluble in alcohol, that the dye cannot now be removed from the fibre by this solvent, and it thus seems probable that it may exist thereon in the form of an acid calcium salt. Thus only by previously steeping the wool in concentrated hydrochloric acid, and subsequently washing, can the colouring matter be extracted by alcohol. The shades given by sanderswood, barwood, and caliaturwood are of a very similar character, camwood, on the other hand, giving somewhat bluer tones, and again according to dyers its colouring matter is more readily dissolved by water than that of the other dyewoods of this class.

	Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Camwood .	Red-violet	Red	Blue-red	Violet
Sanderswood	Brown-red	Orange-red	Red	Maroon

Though now practically unemployed in cotton dyeing, these woods, and especially barwood, were used considerably at one time in the production of a "mock Turkey-red". For this purpose the material was mordanted with a tin mordant, employing either stannate of soda or stannic chloride, and subsequently tannin or sodium carbonate as the fixing agent. On dyeing with barwood, a good bright red colour was thus produced, fast to milling but somewhat fugitive to light.

In wool dyeing, these woods still find a moderate application, usually in conjunction with other dyewoods, such as logwood and fustic, for the production of compound shades, and to a slight extent as a "bottom" in indigo dyeing. The general method of dyeing with them consists in first boiling the wool in a bath containing the wood, and then subsequently adding a solution of either potassium dichromate, ferrous sulphate or copper sulphate, the first operation being known as "stuffing" and the second, in which the shade becomes much browner, "saddening".

The colours given by these dyewoods are somewhat fugitive to light, and thus they have been almost superseded by the alizarins.

SANDERSWOOD.

This dyestuff, known also as *Red Sanderswood*, *Santalwood*, or *Sandelwood*, is the product of the *Pterocarpus santalinus* (Linn.), a papilionaceous tree growing in tropical Asia. It is, or was, imported from the East Indies, Ceylon, the coasts of Coromandel and Malabar, Golconda, Madagascar, etc. It comes into commerce in the form of hard heavy billets of a dull red colour. In the state of powder it gives off a faint aromatic odour like that of orris root, specially noticeable when it is heated or boiled with water. It yields to alcohol about 19·6 per cent. of extract, mainly consisting of colouring matter which is sparingly soluble even in boiling water, though readily in alcohol.

The resinous colouring matter was first isolated from Sanderswood by Pelletier (Ann. chim. phys., 1832, (2), 51, 193), who termed it *sandel red*, and assigned to it the formula $C_1H_{10}O_5$. Meier (Arch. Pharm., 1848, 55, 285; 56, 41) named the colouring matter he obtained *santalic acid* or *santalin*, and though he did not analyse it, considered it to be a purer form of Pelletier's "sandel red". Meier extracted the wood with ether, evaporated the solution, and washed the residue with water. The impure product was dissolved in alcohol, the colouring matter precipitated by means of lead

acetate, and the lead salt was collected and well washed with alcohol. In alcoholic suspension this lead compound was now decomposed by dilute sulphuric acid, and the clear liquid, after removal of the lead sulphate, was evaporated to crystallisation. Thus obtained, the santalin consisted of minute red crystals, melting-point 104°, insoluble in water but very soluble in alcohol. Sulphuric acid dissolved it with a dark red tint and caustic alkalis with a purple colour. Somewhat later Weyermann and Haffely (Annalen, 1850, 74, 226) suggested for santalin the formula $C_{15}H_{14}O_5$, though Franchimont and Sicherer again (Ber., 1879, 12, 14) considered the formula $C_{17}H_{16}O_6$ preferable. These latter authors who adopted a process very similar to that devised by Meier, could not obtain santalin in a crystalline condition, though this melted at 104—105°. Fused with caustic potash the amorphous product gave *acetic acid*, *resorcinol*, and probably also *protocatechuic acid* and *catechol*, and when heated with hydrochloric acid at 180° methyl chloride was evolved. Nitric acid gave oxalic acid and a yellow bitter substance, probably *picric* or *styphnic acid*, and when oxidised with permanganate, a crystalline substance having a strong odour of *vanillin* together with oxalic and acetic acids was produced. Weidel (Zeitsch. für Chem., 1870, 6, 83) extracted the wood with boiling dilute alkali, neutralised the solution with hydrochloric acid and collected and dried the voluminous brick-red precipitate. By long-continued extraction with ether he obtained from this two crystalline substances, *santal*, $2C_6H_6O_3$, $3H_2O$, which is colourless, and a bright red compound, $C_{14}H_{12}O_4$.

Santal crystallised from alcohol in colourless rectangular plates, sparingly soluble in alcohol, soluble in caustic alkaline solutions, with a pale yellow colour. With alcoholic ferric chloride a red coloration was produced. When treated with bromine, a crystalline bromo compound $C_8H_4Br_2O_3$ was obtained, and by fusion with alkali, protocatechuic acid was produced.

The compound $C_{14}H_{12}O_4$, which is very sparingly soluble in boiling alcohol, was obtained as a red crystalline powder possessing a green metallic lustre. It dissolved in caustic alkalis with a reddish-purple colour, and in sulphuric acid with an orange tint. Perkin (Chem. Soc. Trans., 1899, 75, 443) obtained from the commercial santalin of Merck of Darmstadt, by the employment of alcoholic potassium acetate, a potassium salt which on analysis agreed with the formula $C_{30}H_{27}O_5K$.

Cain and Simonsen (Chem. Soc. Trans., 1912, 101, 1061) give two methods for the preparation of santalin from the wood, and also for its subsequent purification. In one case an alcoholic, and in the

second an ethereal extract was employed, and in both instances the colouring matter was isolated by means of its lead salt. The product from the former process was converted into potassium salt and the colouring matter obtained by its decomposition repeatedly crystallised from alcohol, whereas that obtained by the latter method was crystallised only from dilute alcohol. Santalin thus prepared consisted of a bright red micro-crystalline powder which softened at 223° and melted to a deep red oil at 226°. It possessed the formula

$$C_{14}H_{11}O_4OMe,$$

and gave with potassium acetate the salt $C_{20}H_{17}O_{10}K$.

When santalin is acetylated, *diacetylsantalin*, $C_{15}H_{12}O_5(C_2H_3O)_2$, a reddish-brown micro-crystalline powder, is obtained, whereas by acetylation in presence of sodium acetate and zinc-dust a compound $C_{21}H_{20}O_8$, isolated as a pale brown powder, melting-point 242—243°, is produced, and this appears to contain three acetyl groups. Santalin methylated by means of methyl sulphate and aqueous alkali gives *santalin dimethyl ether*, $C_{15}H_{12}O_3(OMe)_2$, a red, micro-crystalline powder, melting-point 165—167°, and a second compound $C_{16}H_{16}O_5$, melting-point 248—250°. The latter is obtained in much larger quantity when the operation is carried out in alcoholic solution.

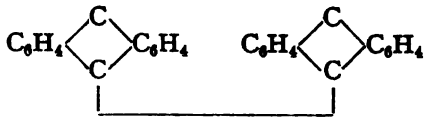
By oxidation with permanganate, santalin dimethyl ether gives *butyric*, *veratric*, and *anisic acids*.

Nitro-diacetyl-santalin, $C_{19}H_{17}O_9N$, scarlet micro-crystalline powder, melting-point 180—181°; *dibenzoyl-santalin*, $C_{29}H_{22}O_7$, brown-red powder; *santalin oxime*, $C_{15}H_{15}O_5N$, red powder; and *benzene-azo-santalin*, $C_6H_5 . N_2 . C_{15}H_{13}O_5$, purple powder, have also been described.

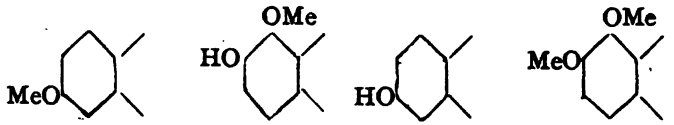
In a later paper (*ibid.*, 1914, 105, 1335) Cain, Simonsen and Smith consider that the formula $C_{15}H_{14}O_5$ originally assigned by them to santalin should be doubled. Thus *santalin monomethyl ether*, the second product of the methylation of santalin referred to above, gives, similarly to the dimethyl ether when oxidised, *anisic* and *veratric acids*, and therefore cannot possess the simple formula $C_{14}H_{10}O_5(OMe)_2$.

Again, by oxidation in the same way, *nitrosantalin dimethyl ether* yields *anisic acid*, 4 *nitro* : 2 : 3-*dimethoxybenzoic acid* and two other acids at present unidentified.

According to Grandmougin, santalin on distillation with zinc-dust yields *anthracene*, and though Cain, Simonsen and Smith were unable to confirm this result, they are inclined to the opinion that it is possibly a di-anthracene derivative, thus—



It is also suggested in their paper that the monomethyl ether yielding as it does anisic and veratric acids, has an unsymmetrical formula in which the two hydroxyls and four methoxy groups are distributed in the four benzene rings as shown below:—



By the reducing acetylation of santalin dimethyl ether the compound $C_{34}H_{32}O_{10}.O.COCH_3$, melting-point 192°, is obtained, and by this reaction one ketonic group appears to have been reduced, and subsequently to have undergone acetylation. *Ethyl-carbanato-santalin*, $C_{30}H_{26}O_{10}(CO_2Et)_2$, a red-brown powder, has also been obtained by these authors.

O'Neill and Perkin (Chem. Soc. Trans., 1918, 113, 125) isolated the colouring matter from an alcoholic solution by means of strong aqueous baryta, thus avoiding the very tedious filtrations involved by the lead acetate method. The crude product thus obtained is submitted to a fractional separation, for which purpose ethyl acetate and ether are mainly employed, and as a result these authors consider that at least two colouring matters, *santalin* and *deoxysantalin*, are present in this dyewood.

Santalin obtained by this method consists of a chocolate-coloured powder which when heated softens at 243°, decomposes at 250—260°, and at 270° is converted into a honeycombed carbonaceous mass. The formula $C_{24}H_{22}O_8$ is proposed for this substance rather than the $C_{30}H_{28}O_{10}$ adopted by Cain and Simonsen, whereas the potassium compound given by potassium acetate is represented either as $C_{96}H_{87}O_{32}K$ or $C_{72}H_{65}O_{24}K$. *Acetylsantalin*, $C_{24}H_{18}O_8(C_2H_3O)_4$ on heating commences to decompose at about 225°, and at 250—260° yields a carbonaceous mass.

Deoxysantalin, the more soluble colouring matter, to which the formula $C_{24}H_{24}O_7$ is tentatively assigned, consists of a bright red powder, the solution of which in ether exhibits a greenish fluorescence. Unlike santalin, the alcoholic solution gives no immediate precipitate with potassium acetate, and only by means of excess of the reagent, or on keeping, does a gelatinous deposit separate. Its colour

reactions, employing alcoholic hydrobromic acid, alcoholic ferric chloride, and sodium hydroxide solution, are of a much yellower character than those given by santalin with these reagents. *Acetyl deoxysantalin*, $C_{24}H_{20}O_7(C_2H_3O)_4$, forms an almost colourless powder very distinct in appearance from acetylsantalin. A molecular weight determination of acetylsantalin employing naphthalene as solvent made by these authors gave the extremely high figure 2558. This approximates to that given in a similar way by acetyl-iso-santalin (*loc. cit.*, Camwood), but the inference to be drawn from these results is doubtful, in that the naphthalene solution may be of a colloidal character. According to O'Neill and Perkin, deoxysantalin is possibly the santalin described by Meyer, and may still contain some impurity which has hitherto prevented its isolation in a crystalline condition. The shades given by santalin and deoxysantalin on mordanted woollen fabrics are of a very similar character to those given by sanderswood itself and are referred to in the article on Camwood.

O'Neill and Perkin point out that the dyeing property of sanderswood seems to be due rather to deoxysantalin than to santalin, and although sanderswood is specially rich in colouring matter, it is astonishing how little of this comes into play during the dyeing process. Proof of this is obtained by dyeing wool with 60 per cent. of sanderswood and at the end of the operation employing the residual wood twice for dyeing fresh material. The first pattern possessed the usual colour, the second was pale pink, and the third was practically undyed, indicating that all the colouring matter soluble in water had then been removed. The woody matter, however, now yielded to alcohol 13·8 per cent. of extract compared with the 19·4 per cent. originally present, and this consisted of a dark red resinous mass and contained much santalin. Even, therefore, if it be presumed that all the soluble matter removed from the wood in the dye-bath is colouring matter (and this is improbable), it is evident that the larger proportion present therein, owing to its insoluble nature, remains undissolved and takes no part in the operation. Attempts to isolate Weidel's compounds (*loc. cit.*) from sanderswood were unsuccessful.

In addition to colouring matter, sanderswood contains two neutral compounds, *Ptero-carpin* and *Homo-ptero-carpin*, which were first isolated by Cazeneuve and Hugonueng (Comptes rendus, 1874; civ., 1722). These authors extracted a dried mixture of the wood and slaked lime with ether, and the product which remained on evaporating the ether was crystallised, first from alcohol and then fractionally so from carbon disulphide.

Ptero-carpin, the more sparingly soluble compound, and to which the formula $C_{20}H_{16}O_6$ was assigned, consisted of colourless plates, melting with previous softening at 152°. It was insoluble in alkalis and acids and possessed the specific rotatory power of $[\alpha_j] = -211$. By the action of bromine, in presence of carbon disulphide, it yielded *brompterocarpin*, $C_{20}H_{15}BrO_6$, and this crystallised from a mixture of alcohol and benzene in fine needles. Smith (Philippine Journal of Science, 1910, v., 451) has, however, shown that the correct formula of pterocarpin, also present in Narrawood, is $C_{14}H_{12}O_4$, and its melting-point 163°.

According to Cazeneuve and Hugonueng, *Homopterocarpin*, which is somewhat readily soluble in carbon disulphide, melts at 82—86°, has the formula $C_{24}H_{24}O_6$, and in an approximately 5 per cent. solution in chloroform, its specific rotation is $[\alpha_j] = -199$. By bromination it yielded *bromhomopterocarpin*, $C_{24}H_{23}BrO_6$, amorphous, and *hexabromhomopterocarpin*, $C_{24}H_{18}Br_6O_6$, crystallising in plates, whereas with nitrous acid an unstable *nitroso* derivative, $C_{24}H_{23}(NO)O_6$, was obtained. Fuming nitric acid gave *trinitro-orcinol* and fusion with potassium hydroxide *phloroglucinol*. When heated with hydriodic acid, methylic iodide was evolved, and was evidence of the presence of methoxy groups.

Brooks (*loc. cit.*), who also isolated homopterocarpin (melting-point 86°) from Narrawood, has assigned to it the formula $C_{17}H_{16}O_4$, and finds that when fused with alkali it gives *resorcinol*, and when distilled with zinc-dust *resorcinol dimethyl ether*. Ryan and Fitzgerald (Proc. Roy. Irish Acad., xxx., 1913, 106), who obtained homopterocarpin (melting-point 88°) from barwood, also adopted the formula $C_{17}H_{16}O_4$, but could only obtain from it a *dibrom derivative*, $C_{17}H_{14}Br_2O_4$, which crystallised in colourless needles, melting at 200°. Contrary to Cazeneuve's statement it contains no methoxy group, but nevertheless a phenolic substance is obtained from it by the action of hydriodic acid. Again, the specific rotatory power previously assigned to it by the latter author is too low, and in an approximately 4 per cent. solution in chloroform is $[\alpha_D]$ 20° C. = −211°. Ryan and Fitzgerald consider it possible that homopterocarpin is derivative of chromane or cumarane.

Barwood.

Barwood is the wood of a large, fine tree, *Baphia nitida* (Lodd.), and is imported from the west coast of Africa, e.g. Sierra Leone, Angola, etc. In the log its physical properties are generally similar to

those of sanderswood; in the rasped condition it has a somewhat brighter red colour and is devoid of aromatic odour. According to Girardin and Preisser, boiling water extracts about 7 per cent. of colouring matter, alcohol about 23 per cent., and hydrated ether about 19 per cent.

Anderson (Chem. Soc. Trans., 1876, ii., 582) extracted ground barwood with anhydrous methylated ether free from alcohol. By spontaneous evaporation of the concentrated ethereal solution a small quantity of *baphic acid* is deposited in the form of tabular crystals. After further evaporation, mixing the concentrated extract with alcohol, and allowing to stand for some days, there is deposited a crystalline magma of *baphiin* contaminated with a solid red colouring matter and some dark viscous colouring matter not yet examined.

After exhaustion with ether the wood is extracted with alcohol, and after concentrating the solution it is left at rest for some time, when it congeals to a semi-crystalline mass which contains a viscous red colouring matter and a crystalline constituent not examined.

Baphiin, $C_{24}H_{20}O_8$ (melting-point about 200°), crystallises from alcohol in the form of lustrous tabular crystals having an odour of orris root; from ether it crystallises in tufts of needles. It is insoluble in water, and very sparingly soluble in benzene or in carbon disulphide. In alcoholic solution it rapidly oxidises on exposure to air, producing orange-red or pale purple colours.

Baphic acid, $C_{24}H_{22}O_9$ or $C_{24}H_{22}O_{10}$, is prepared by boiling baphiin with dilute caustic potash, and adding hydrochloric acid, when it is thrown down as a yellowish-white precipitate. Crystallised from ether it forms white nacreous scales, very soluble in ether, slightly less so in alcohol, and insoluble in water (cf. Santal).

Baphinitin, $C_{24}H_{24}O_6$, is thrown down as a crystalline precipitate on the addition of water to the filtrate from the precipitate of lead baphate which is formed on mixing alcoholic solutions of baphiin and lead acetate. It is also the chief product of the action of boiling dilute caustic potash on baphiin. Baphinitin forms white needles, soluble in alcohol or in ether, but insoluble in water; it has the same odour as baphiin but stronger (cf. Pterocarpin).

Baphinitone, $C_{26}H_{26}O_6$.—On boiling baphiin with a strong aqueous solution of caustic potash without access of air, an insoluble residue is left which contains three substances: (1) baphinitin, moderately soluble in alcohol or ether; (2) baphinitone, very readily soluble in these liquids; (3) a small quantity of an unexamined substance, melting-point 164·1°, very sparingly soluble even in hot alcohol, and separating therefrom in granular crystals. . Baphinitone

is extracted from the above-mentioned residue insoluble in caustic potash, by treating it with cold alcohol, in which it readily dissolves along with a very small amount of baphinitin. The solution is evaporated, and the treatment with alcohol is repeated until the crystals thus obtained, after drying over sulphuric acid, have a melting-point of about 88°. Baphinitone crystallises from alcohol in hemispherical masses composed of white lustrous radiating crystals insoluble in water (cf. Homopterocarpin).

Tribromo-baphinitone, $C_{26}H_{22}Br_3O_6$, is obtained by mixing ethereal solutions of baphinitone and bromine; on evaporating off the ether it remains as a white substance, which may be purified by washing with alcohol or ether, in which it is almost insoluble. It separates from a hot ethereal solution in small granules, which melt with blackening at 180·2°.

Baphiin, baphinitone, and substance (3) above referred to, are all coloured orange-yellow by sulphuric acid; with nitric acid an orange-red colour is obtained, which changes gradually to green.

In addition to the above-mentioned substances, barwood contains, according to Anderson, at least three colouring matters: Ether extracts from the wood two of these; one (*a*) which is less soluble, and which tenaciously adheres to the baphiin, and another (*b*) which is crystalline and is easily removed from it. When the extraction with ether is completed, alcohol will dissolve out a third colouring matter (*c*). All are insoluble in benzene, and give purple lakes with lead acetate, and purple solutions with alkalis.

O'Neill and Perkin (*loc. cit.*) worked up barwood by the same methods they had previously applied to sanderswood, and isolated a colouring matter corresponding with the santalin of this latter. This, which consisted of a chocolate-red powder, possessed the formula $C_{22}H_{16}O_5(OCH_3)_2$, and, on heating, commenced to soften at 240°, apparently decomposing, and at 270° had the appearance of a honeycombed carbonaceous mass. Its colour reactions are the same as those given by santalin, and it thus appears probable that the two compounds are identical.

When the crude colouring matter of barwood, dissolved in alcohol, is poured into ether the main bulk of the santalin is precipitated. The ethereal liquid now contains, in addition to a colouring matter resembling *deoxysantalin*, two crystalline substances identical with those previously stated by Weidel (*loc. cit.*) as present in sanderswood. To isolate santal the ether solution is treated with hydrobromic acid to remove colouring matter, the colourless crystalline residue remaining after evaporation is washed with benzene, and

recrystallised first from dilute and subsequently from absolute alcohol.

The analytical figures given by this compound agree with those obtained by Weidel, but methoxy determinations show that its formula is to be represented as $C_{15}H_9O_5(OCH_3)$, and not $C_8H_6O_3$, as proposed by this author.

Santal, which seems to be very similar to Anderson's baphic acid, melts at 222—223°, is readily soluble in dilute alkali hydroxides, and sparingly so in absolute alcohol from which it crystallises in thin plates or flat needles. With alcoholic lead acetate it gives a colourless precipitate, and with alcoholic ferric chloride a violet-black coloration, although this, according to Weidel, is dark red. By the action of hydriodic acid santal is converted into *santol*, probably $C_{15}H_{10}O_6$, which consists of small colourless flat needles, melting-point 270—273°. Its solution in dilute alkali hydroxide, at first colourless, rapidly develops a reddish-violet tint, and the liquid on acidification deposits yellow crystals. If the acid mixture is boiled these become colourless, apparently with regeneration of santol, for when collected and washed the product can again be made to produce the same changes. Santol thus appears to contain a lactone group. The hydrobromic acid liquid obtained during the isolation of the santal, was diluted with water, the precipitated colouring matter dissolved in a little ethyl acetate, the solution being allowed to evaporate spontaneously. Minute crystals were slowly deposited, and these were collected and digested with absolute alcohol to remove santal. This compound, evidently Weidel's substance $C_{14}H_{12}O_4$, and now termed by O'Neill and Perkin *santalone*, is sparingly soluble in most organic solvents, and crystallises from alcohol in small red leaflets. It is soluble in dilute alkalis with a red colour, whereas alcoholic ferric chloride colours it a violet tint. As obtained by these latter authors its complete purity was doubtful, but the purest preparation obtained darkened about 280° and melted at 300°. Its true formula is probably either $C_{22}H_{18}O_4(OCH_3)_2$ or $C_{22}H_{16}O_4(OCH_3)_3$, and in case this is correct this compound has the composition of a *deoxysantalinmonomethyl ether* with which its general properties are in harmony.

Ryan and Fitzgerald (Proc. Roy. Irish Acad., 1913, 5, 106), employing the following method, have isolated *homopterocarpin* from barwood. The ground material was percolated for a few days with warm alcohol, then with ether and finally with chloroform. The residue obtained by evaporating these extracts was exhausted with ether, the ethereal solution washed with dilute alkali and then

distilled. The product, when recrystallised from alcohol, formed colourless acicular crystals, melting-point 84°, and was identical with the baphinitone of Anderson and the homopterocarpin existing in sanderswood.

A fuller account of this compound, which possesses the formula $C_{17}H_{16}O_4$, is given in the article describing the latter dyewood. It is very probable, again, that the *baphinitin* described by Anderson as existing in barwood is pterocarpin.

Caliaturwood.

This wood, the botanical origin of which appears to be unknown, is very similar to though somewhat darker in colour than sanderswood. It was imported from the East Indies and is stated to have been chiefly employed on the Continent. According to Franchimont and Sicherer (*loc. cit.*) it contains santalin but in larger amount than sanderswood.

Narrawood.

Narrawood, *Pterocarpus spp.*, a well-known Philippine wood, according to Brooks (Philippine Journal of Science, 1910, v., 448), contains constituents very similar to those of sanderswood. To isolate the red colouring matter, the wood shavings were extracted with alcohol, the alcoholic extract concentrated and three volumes of water added. The solution was boiled to remove alcohol, and the red amorphous mass, which had then separated, was digested with about five parts of chloroform.

Thus obtained, *Narrin* consisted of a dark red amorphous powder, readily soluble in alcohol and insoluble in chloroform, which could not be obtained in a crystalline state. According to Brooks it is not identical with the santalin of sanderswood, for a preparation of this melted at 104°, whereas narrin does not melt but swells with charring about 180°. When fused with alkali narrin gives *phloroglucinol* and *resorcinol*, and by a slow oxidation with permanganate 12 grams gave 0·5 gram of a substance possessing a strong odour of *vanillin*. That it consisted of this substance was confirmed by its conversion into the phenylhydrazone which melted at 104°. By distillation with zinc-dust narrin yields a small amount of *resorcinol dimethyl ether*. Narrin, like santalin, gives with alcoholic potassium acetate a precipitate of potassium salt, and the copper salt prepared in this way with copper acetate had the composition $(C_{15}H_{12}O_5)_2Cu$.

The dyeing properties of narrin are similar to those of santalin, but the shades produced are not very fast to soap.

In addition to colouring matter, Brooks isolated from narrawood both *ptero-carpin* and *homoptero-carpin*. By a careful examination of these substances he concluded that the formulæ previously assigned to them is incorrect, and should in reality be, respectively, $C_{14}H_{12}O_4$ and $C_{17}H_{16}O_4$ (see "Sanderswood").

Camwood.

Camwood or "cambe wood," stated to be derived from a variety of *Baphia nitida* (cf. barwood), is very similar in general properties to the "insoluble red" dyewoods already described. It is, however, more expensive, yields deeper shades on dyeing, and its colouring matter is said to be more soluble than that present in the other woods.

It has been recently examined by O'Neill and Perkin (Chem. Soc. Trans., 1918, 113, 126), who employed for this purpose similar methods to those found serviceable with sanderswood (*loc. cit.*).

Iso-santalin, the main colouring matter, forms a chocolate-coloured powder, which on grinding becomes redder in appearance, and is readily soluble in boiling methylated spirit. When heated, it shows no sign of melting, darkens at 280°, and is fully decomposed at 290—300°, being then a carbonaceous powder. It possesses the formula $C_{22}H_{16}O_6(OCH_3)_2$, gives with alcoholic potassium acetate the salt $C_{96}H_{83}O_{32}K$ or $C_{72}H_{65}O_{24}K$, shows evidence of the formation of soluble oxonium salts, and in general properties closely resembles its isomer santalin. The colour reactions and also the dyeing properties of the two compounds indicate, however, that they are distinct substances:—

	Santalin.	*Iso-santalin.*
Alcoholic hydrobromic acid . .	Crimson.	Reddish-violet.
Dilute sodium hydroxide . . .	Dull red.	Dull violet.
Alcoholic ferric chloride . . .	Violet.	Bluish-violet.

For dyeing the colouring matter in alcoholic solution was added to the water in the dye-bath and the dyeings were carried out (*a*) employing wool alone, (*b*) employing wool alone and subsequently saddening with bichrome, (*c*) employing wool mordanted with bichrome and cream of tartar, and (*d*) employing wool mordanted with bichrome and sulphuric acid.

	(*a.*)	(*b.*)	(*c.*)	(*d.*)
Santalin .	Pale dull red.	Dull reddish-brown.	Pale reddish-pink.	Pale red-pink.
Iso-santalin	Pale violet-red.	Dull violet-maroon.	Violet-red.	Violet-red weaker than (*c*).

Acetyl-iso-santalin, $C_{24}H_{18}O_8(C_2H_3O)_4$, consists of a deep salmon-coloured powder, and does not possess a definite melting-point, being gradually decomposed without fusion between 250—280°. A molecular weight determination employing naphthalene gave the high figure 2344, a result very similar to that given in these circumstances by acetyl-santalin itself, and which may possibly be due to the production of a colloidal solution.

Deoxy-iso-santalin, $C_{24}H_{18}O_5(OCH_3)_2$, corresponding to the deoxysantalin of sanderswood, is a scarlet amorphous powder which has not yet been obtained in a definitely crystalline condition. When heated, it did not show a distinct melting-point but decomposed at 160—165° with evolution of gas. A solution of this substance in absolute alcohol gives no immediate precipitate with potassium acetate, as happens in the case of iso-santalin, and only when excess of the reagent is employed is a gelatinous deposit formed.

A comparison of the colour reactions and dyeing properties of deoxy-iso-santalin (*a*) and deoxy-santalin (*b*) is given in the following table:—

	(*a.*)	(*b.*)
Alcoholic solution . . .	Orange.	Orange-brown.
Alcoholic hydrobromic acid .	Bright crimson.	Scarlet.
Dilute sodium hydroxide .	Crimson-scarlet.	Scarlet.
Alcoholic ferric chloride .	Violet.	Maroon.

The dyeing experiments were carried out by the same methods as those described above.

	(*a.*)	(*b.*)	(*c.*)	(*d.*)
Deoxy-iso-santalin	Pale red-violet.	Red puce.	Dull red-violet.	Pale dull red-violet.
Deoxy-santalin .	Red.	Dull bluish-red.	Dull crimson.	Red.

Acetyl-deoxy-iso-santalin, $C_{24}H_{30}O_7(C_2H_3O)_4$, when heated, fused and decomposed at 170—175°. It consists of an almost colourless powder differing considerably in appearance from acetyl-iso-santalin,

A molecular weight determination, employing naphthalene as solvent, gave the figure 1324, which is approximately half that found in the same circumstances for acetyl-iso-santalin.

By exhaustion with alcohol the sample of camwood employed by these authors gave 16 per cent. of extract.

Camwood does not appear to contain either ptero-carpin or homoptero-carpin.

Red Dura.

The "Red Dura" or "Durra" of the Soudan, also known as "Shikytan," consists of the deep reddish-brown sheaths of a grass, apparently the *Andropogon sorghum* (Brot.), var. *vulgaris*, also known as the *Sorghum vulgare* (Pers.) or "Great millet," the grain of which provides so important a foodstuff. According to E. P. Brown, Inspector of the Blue Nile Province, the "Shikytan" is used for producing a red dye, practically utilised for staining a grass called "lanzura," employed in the manufacture of coloured "bursh" mats, but occasionally for the leather of "markubs" (Sudanese shoes). It is specially grown for dyeing purposes. A full account of the *S. vulgare* is given by Watt ("Dictionary of Economic Products of India," 6, [iii.], 289). The grain occasionally possesses a brick-red colour, and that at Harihar is used for preparing a red morocco from goat skin. The canes of *S. saccharatum* also, when pressed and allowed to ferment, develop a red or reddish-brown colour, and the dye thus produced can be extracted by means of dilute alkali. The Indian, Persian, Abyssinian, and Egyptian forms would seem to be derived from the *A. sorghum*, var. *durrha;* but the fact that this plant is so extensively cultivated in Egypt as a foodstuff and the "Shikytan" is grown entirely for dyeing purposes, seems to indicate that this latter is again a special variety.

The colouring matter, *durasantalin*, to which the formula $C_{16}H_{12}O_5$ has been provisionally assigned (Perkin, Chem. Soc. Trans., 1910, 97, 220), consists of a bright red or scarlet powder, possessing an ill-defined crystalline structure. It is soluble in alkalis with a red-violet colour, passing rapidly to brown on air oxidation, gives with alcoholic ferric chloride a brown liquid, and when fused with alkali, *p-hydroxybenzoic acid* and *phloroglucinol*, together with a trace of a third substance, probably *p-hydroxyacetophenone*, are produced. Durasantalin does not dye mordanted calico, but behaves as a substantive dyestuff towards wool upon which it produces a dull-red shade. A very permanent and slightly fuller colour can be produced by previously mordanting the wool with chromium. In some respects

this dye resembles the santalin of sanderswood, but there can be no doubt that these substances are chemically distinct.

Safflower (Bastard Saffron).

This dyestuff consists of the dried florets of *Carthamus tinctorius* (Linn.), an annual thistle-like plant belonging to the *Cynarocephalæ*. A native of Southern Asia, it has been cultivated in China, India, Persia, Egypt, also in central and southern Europe. When in full bloom the yellow florets are plucked, and either at once dried, so as to form an orange-coloured fibrous mass somewhat resembling saffron, or they are first kneaded with water, in order to remove a useless yellow colouring matter, and then pressed into the form of lens-shaped cakes and dried.

Safflower owes its value to an insoluble red colouring matter which occurs only in very small amount, about 0·5 per cent., whereas the soluble yellow colouring matter is said to be present to the extent of about 30 per cent.

The yellow colouring matter may be obtained by first precipitating a cold aqueous extract of safflower with lead acetate and acetic acid and then adding ammonia to the filtrate, i.e. precipitating with basic lead acetate. The second precipitate thus obtained is carefully decomposed with dilute sulphuric acid, and after removing the lead sulphate the filtrate is evaporated to dryness with exclusion of air. It is thus obtained as an amorphous substance, having acid properties, a bitter taste, and a peculiar odour. It is of a very unstable character, and on exposure to air seems to oxidise, becoming brown and partially insoluble in water. According to Schlieper, its composition is represented by the formula $C_{16}H_{20}O_{10}$; according to Malin, it is $C_{24}H_{30}O_{15}$. This product is apparently a glucoside or contains a substance of this character, for after digestion with boiling dilute sulphuric acid, the solution yields to ether a small quantity of a crystalline yellow colouring matter (Perkin, private communication).

Carthamin or *carthamic acid* is the name given to the useful red colouring matter, which, although insoluble in water, is readily soluble in alkaline solutions. To obtain it, safflower is well washed with slightly acidified water to remove the yellow colouring matter, then it is steeped for some time in a cold dilute solution of sodium carbonate. If the alkaline solution be now acidified with acetic or tartaric acids the carthamin is precipitated in so finely divided a condition that it cannot be successfully collected. This difficulty is, however, obviated by making use of the fact that carthamin is readily attracted and removed from its acidified solution by cellulose.

Hence bleached cotton is immersed and moved about in the alkaline solution, which is at the same time gradually acidified with tartaric or citric acid.

In this manner the carthamin is slowly precipitated and is at once attracted by the cotton, which thus becomes dyed red. After washing the dyed cotton with slightly acidified water, the colouring matter is dissolved off by means of a dilute solution of sodium carbonate, from which the carthamin is thrown down, on the addition of tartaric acid, as a bright-red precipitate, which is now in a purer and more granular form. Further purification is effected by dissolving the dried precipitate in alcohol and reprecipitating with water.

Preisser, the first to investigate carthamin (J. pr. Chem., 1844, [i.], 32, 142), described this substance as colourless needles, which, by air-oxidation in the presence of alkali, were converted into carthamein, the true colouring matter. Schlieper (Annalen, 1846, 58, 357), however, proved that Preisser's statements were incorrect, and he isolated carthamin in the form of green iridescent red crusts, or as a granular greenish-red powder, to which he assigned the formula $C_{14}H_{14}O_7$. When digested with boiling alcohol, it was converted into a yellow compound having the composition $C_{14}H_{14}O_6$. According to Malin (Annalen, 1840, 36, 117), carthamin gives *p*-hydroxybenzoic acid when digested with boiling potassium hydroxide solution.

Radcliffe (J. Soc. Dyers, 1897, 13, 158), by extracting an air-dried commercial paste extract of safflower with methyl alcohol, subsequently evaporating the solution, and adding hot water, obtained a product crystallising in red, iridescent needles, melting at 168—169° (provisional), which, when exposed to sunlight, changed to a red powder. A study of the absorption spectra of solutions of the carthamin,* and an account of its general properties, are described in his paper, but the author reserved analytical details for a later communication.

Kametaka and Perkin (Chem. Soc. Trans., 1910, 97, 1415) prepared carthamin in a crystalline condition. The dried and finely ground commercial extract of safflower is extracted on the water-bath with successive quantities of pyridine, and the combined extracts are evaporated to a small bulk under reduced pressure. Warm water is then added until a faint turbidity occurs, and on standing a semi-solid crystalline mass is obtained, which is collected and washed with water. To remove a wax the crystals are digested first with chloroform and then with ether, and the product is purified by

* According to Kametaka and Perkin this compound is a salt of carthamin rather than the colouring matter itself.

repeated crystallisation from pyridine and water. When crystallised in this manner carthamin contains pyridine of crystallisation, which is best removed by drying the substance at 125° to 160°.

Carthamin consists of bright scarlet-coloured prismatic needles which melt and decompose at about 228—230°, is very sparingly soluble in methyl and ethyl alcohols, and insoluble in ether. It dissolves in cold dilute alkali hydroxides, sodium carbonate, and ammonia with an orange colour, and is reprecipitated by acids unchanged. With sulphuric acid carthamin forms a dull red coloured solution, which after heating to 100°, gives with water a violet precipitate, possessing feeble mordant dyeing properties, and is soluble in alkalis with a green coloration. Carthamin is decomposed by heating with dilute mineral acids with formation of a dull brown precipitate. The formula of carthamin is, or closely approximates to, $C_{25}H_{24}O_{12}$, and the anhydrous substance is extremely hygroscopic and takes up two molecules of water of crystallisation.

Monopotassium carthamin, $C_{25}H_{23}O_{12}K$, is formed when the finely powdered colouring matter suspended in boiling alcohol is treated with strong aqueous potassium acetate solution. It consists of green iridescent needles, and is decomposed by hot water with liberation of the free colouring matter.

Benzoyl-carthamin, $C_{25}H_{17}O_{12}(C_7H_5O)_7$, consists of a pale red amorphous powder which melts and decomposes at about 230—235°, and an *acetyl* derivative has been prepared, the analysis of which agrees fairly well with the formula $C_{25}H_{17}O_{12}(C_2H_3O)_7$.

On account of the extreme sensitiveness of carthamin to alkali (see later), it does not appear to be possible to obtain a pure methylation product of this colouring matter by the ordinary methods, and the employment also of diazomethane has not given a successful result.

With nitric acid carthamin yields *picric acid*, and when fused with alkali *p-hydroxybenzoic* and acetic acids are formed. By the action of boiling potassium hydroxide solutions varying in strength from 50—1 per cent. a brownish-yellow coloured liquid was quickly produced, which on neutralisation gave a brown precipitate, not susceptible to crystallisation. The filtrate from this was found to contain *p-coumaric acid* and *p-hydroxybenzaldehyde*. No third product soluble in ether could be obtained by this reaction.

When carthamin in 1 per cent. sodium carbonate solution is treated with hydrogen peroxide *p-coumaric acid* is produced, and the crude methylation product of the colouring matter similarly treated gives *p-methoxycinnamic acid*. By oxidation with chromic acid *anisic acid* and *anisic aldehyde* are obtained.

Kametaka and Perkin were unable to prepare the yellow compound which, according to Schlieper (*loc. cit.*) and Radcliffe (*loc. cit.*), is produced by boiling carthamin with alcohol, and consider that the pure substance does not give this reaction. By boiling the colouring matter with alcoholic aniline, however, a yellow crystalline substance, *aniline xanthocarthaminate*, $C_{25}H_{24}O_{12} . C_6H_7N$, is readily formed. It consists of needles decomposing at 276—278°, sparingly soluble in alcohol. In a similar manner *β-naphthylamine xanthocarthaminate*, $C_{25}H_{24}O_{12} . C_{10}H_9N$, orange-coloured leaflets, decomposing at about 266—268°, can be prepared, and the corresponding *ψ*-cumidine derivative, orange-coloured leaflets, decomposes at about 290°.

These compounds are probably the salts of an acid which is termed *xanthocarthaminic acid;* it appears to be isomeric with carthamin, and is probably closely related to it. It was observed that when the *β*-naphthylamine compound is dissolved in potassium hydroxide solution, the clear yellow liquid becomes cloudy with separation of *β*-naphthylamine. When this latter is removed, and the alkaline liquid is neutralised with hydrochloric acid, a curdy yellow precipitate slowly separates, and this on standing gradually becomes red coloured, a change which is probably due to the reproduction of carthamin. On account of the large amount of oxygen which carthamin contains it is considered possible that an aliphatic nucleus may be present in this colouring matter.

Previous to the discovery of safranine and of the eosins, safflower was frequently used for the production of brilliant pinks or reds, chiefly on cotton or silk. The mode of dyeing is practically the same as that already given in describing the process of obtaining carthamin. The safflower in bags is well washed with cold water, in order to remove the yellow colouring matter, and the red colouring matter is then extracted by a treatment with a cold dilute solution of sodium carbonate. In this solution the material to be dyed is worked about, at the same time adding "lime juice" (citric acid) gradually until in slight excess. Safflower extract is applied in a similar manner.

Dyers usually gave the washed safflower several successive treatments with alkali, employing at first weak and afterwards strong alkaline solutions. The weak solutions give the brightest and purest tints; hence very delicate colours were dyed with these alone, whilst full colours were first dyed with the inferior extracts, and then "topped" or "bloomed" by a dyeing in the purer solutions. The shades obtained from safflower were at one time considered to be

the finest and most delicate a dyer could produce. On the other hand, they were not only expensive but had the disadvantage of being extremely unstable.

Safflower is a very weak dyestuff, for 4 oz. are necessary to dye 1 lb. of cotton light pink, 8 oz. for a rose-pink, and about 1 lb. to produce a full crimson.

It is now rarely, if ever, employed in Europe as a dyestuff, but large quantities are still cultivated, more especially in India, and used for dyeing and pigment manufacture in the East.

Carthamin was sold in a more or less pure condition as a thin aqueous paste, under the name of safflower extract or safflower carmine, but this product is now difficult to obtain in Europe. On the other hand, considerable quantities are still manufactured in Japan, where it is very largely employed as a cosmetic. Carthamin ground up with starch, talc, etc., is used as rouge.

For other references, *v.* Dumas, Annalen, 27, 147; Liebermann, Ber., 7, 247; 8, 1649; Dobereiner, J. Phys. Chem., 26, 266; Salvetat, Ann. Chim. Phys., (3), 25, 337; J. pr. Chem., 44, 475; Dufour, Ann. Chim. Phys., 48, 283.

Species of Coprosma.

The bark, and more especially the roots, of the *C. grandiflora*, *C. linariifolia*, and *C. areolata*, which belong to the natural family of the *Rubiacæ*, and are widely distributed in New Zealand, possess tinctorial property (Aston, New Zealand, J. Sci. Tech., 1918, 1, 3), and being related to madder probably contain either alizarine itself or an allied colouring matter. Thus an alcoholic extract of the *C. grandiflora* is coloured purple by alkali, and becomes yellow on addition of acid. From the acid solution, by means of ether, an orange-yellow crystalline substance can be isolated in small amount.

Kamala.

Kamala or Kamela is the orange-red powder which exists as a glandular pubescence on the exterior of the fruits of the *Mallotus phillipinensis*, Muell. (*Rottlera tinctoria*, Roxb.), a small evergreen tree, met with throughout tropical India, Burma, and Ceylon, also in Java, China, the Malay Islands, and Australia. The ripe capsules are gathered in February or March, and shaken in bags until the powder separates.

Kamala is employed by the Hindoos as an antithelmic drug and for dyeing silk and wool a bright orange colour. The fabric

is dyed in a boiling bath containing 4 parts kamala, 1 part alum and 2 parts sodium carbonate (native barilla), previously well-rubbed together in the powdered state with a small quantity of oil of sesamum. The alum is sometimes omitted, but the addition of alkali is absolutely necessary in order to dissolve the colouring matter, which is of a resinous character and quite insoluble in water. Kamala is also apparently used for the adulteration of annatto, for according to Perkin (private communication), samples of calico obtained from India and presumably dyed with kamala have proved on examination to owe their colour partially if not entirely to annatto. Kamala was formerly employed in this country as a remedy for *taenia*, but appears now to be very little used for this purpose.

Anderson was the first chemist to investigate kamala (Edin. New Phil. J., 1, 300), and he isolated from it by means of ether a crystalline compound *rottlerin*, $C_{11}H_{10}O_3$, a wax, $C_{30}H_{24}O_4$, and a resin melting below 100°, to which he gave the formula $C_{20}H_{20}O_7$. Leube (Jahres., 1860, 562) was unable to obtain any crystalline product from this drug, but he describes two resins, $C_{15}H_{18}O_4$, melting-point 80°, and $C_8H_{12}O_4$, melting-point 191°. Oettingen (Dissert. St. Petersburg, 1862) also could not obtain any crystalline substance from kamala. A. and W. Perkin (Ber., 1886, 19, 3109), however, isolated the crystalline rottlerin ("mallotoxin") of Anderson, and its existence was subsequently confirmed by Jawein (Ber., 20, 182).

As the result of a more extended examination of kamala and employing carbon disulphide for the extraction, A. G. Perkin (Chem. Soc. Trans., 1893, 63, 975) isolated not only Anderson's compounds, but small quantities of two crystalline substances, homorottlerin, which is yellow, and *iso*rottlerin, a salmon-coloured powder, together with a high melting resin.

Rottlerin, $C_{23}H_{20}O_8$ (Perkin, *ibid.*, 1895, 67, 230), salmon-coloured plates, melts at 191—191·5° (Perkin), 200° (Jawein), 202—204° (Telle, Arch. Pharm., 1906, 244, 441), readily soluble in ether. Solutions of the alkali carbonates and hydroxides dissolve rottlerin, the former only on gently warming. On boiling these orange-coloured liquids, decomposition gradually takes place, an odour of benzaldehyde is evolved and a resinous product separates. An alcoholic solution of rottlerin is coloured brown on the addition of ferric chloride.

Acetylrottlerin $(C_{11}H_8O_3(C_2H_3O)_2)_2$, yellow crystalline powder, melting-point 130—135° (Perkin), and *benzoylrottlerin*,

$$C_{23}H_{24}O_9(C_7H_5O)_6,$$

yellow powder (Bartolotti, Gazzetta, 24, [ii.], 480), have been prepared.

Rottlerin forms the following salts: $C_{32}H_{29}O_9Na$, H_2O, orange-brown glistening leaflets; $C_{32}H_{29}O_9K$, H_2O, leaflets; $(C_{32}H_{29}O_9)_2Ba$, minute reddish-brown prisms; $(C_{32}H_{29}O_9)_2Sr$, $(C_{32}H_{29}O_9)_2Ca$, and $C_{32}H_{29}O_9Ag$, fine yellow needles.

Fused with alkali, rottlerin gives *benzoic acid*, *acetic acid*, and *phloroglucinol* (Perkin), and when oxidised with hydrogen peroxide in alkaline solution, *benzaldehyde* and *benzoic acid* are produced. With potassium permanganate (Bartolotti) benzoic acid is also formed. Nitric acid (specific gravity 1·5) gives *p-nitrocinnamic acid*, *o-nitrocinnamic acid*, *p-nitrobenzaldehyde*, and *p-nitrobenzoic acid* (Perkin). When heated with 2 per cent. sodium carbonate solution, a compound termed *rottlerone* separates (Perkin), which crystallises in garnet-red prisms, and to which the formula $C_{29}H_{26}O_6$ has been provisionally assigned.

According to Telle, if rottlerin is heated for ten minutes with barium hydroxide solution, *phloroglucinolmethylether*, a resinous substance and *ψ-rottlerin*, melting-point 235°, are produced. When heated for ten minutes with zinc powder and sodium hydroxide, rottlerin gives 60 per cent. of resin and about 30 per cent. of phenols, also *β-phenylpropionic acid*, acetic acid, and a small quantity of a crystalline acid, melting-point 185—185·5°. From the mixture of phenols, *phloroglucinolmonomethylether* and *phloroglucinoldimethylether* were isolated. *Phloroglucinoltrimethylether* and a camphor-like substance, melting-point 170—172°, were produced, when, with the zinc powder, only 2 per cent. sodium hydroxide solution was employed. The molecular weight of rottlerin, determined cryoscopically in naphthalene, was 486, and agrees with that assigned to this substance by Perkin (*loc. cit.*).

Homorottlerin, $C_{33}H_{30}O_9$ (?), pale yellow needles, melting-point 192—193°, is present in exceedingly small amount in kamala. It differs from rottlerin in being much less soluble in toluene, chloroform, or acetic acid, but otherwise the properties of these two compounds are similar (Perkin).

iso-Rottlerin, $C_{12}H_{12}O_6$ (?), has been obtained in the form of plates, melting-point 198—199°, insoluble in hot benzene, carbon disulphide, or chloroform. Cold solutions of the alkali carbonates dissolve it readily, and these solutions when boiled do not deposit resinous matter or emit an odour of benzaldehyde, as is the case with the alkali salts of rottlerin itself. It is probable that this compound, very little of which has been yet obtained, may prove to consist of hydroxyrottlerin (Perkin).

The low-melting resin of Anderson, $C_{30}H_{30}O_7$ (?), $C_{12}H_{12}O_3$ (?),

(Perkin), consists of a brittle transparent dark red mass, melting below 100°, and is readily soluble in carbon disulphide, ether, or chloroform. With hot alkaline solutions, it behaves similarly to rottlerin and evolves an odour of benzaldehyde, and with nitric acid (specific gravity 1·5) gives *p*-nitrobenzoic acid. Perkin's *high melting resin* is a pale straw-coloured mass, melting-point about 150°, and in general properties resembles the low-melting variety.

According to Hummel and Perkin (J. Soc. Chem. Ind., 1895, 14), for silk dyeing it is best to add 1 part of kamala and 0·5—1 part sodium carbonate to boiling water, then to enter the silk and to dye at the boiling temperature for two to five minutes only. Other experiments indicated that the amount of sodium carbonate to employ should be regulated by the quantity of water used rather than by that of the kamala, namely, at the rate of 13—14 grams (Na_2CO_3, 10 aq) per litre. After dyeing for a short time with the addition of alkali only, to the extent of one-fifth of the weight of the kamala used, the addition of alum or stannous chloride to the dye-bath makes the colour fuller and more orange. A similar but by no means identical effect is obtained by making a slight addition of sulphuric acid.

As pointed out by Perkin (*loc. cit.*), rottlerin is decomposed by boiling sodium carbonate solution, and the colour ultimately fixed on the fibre most probably consists of rottlerone. Although rottlerin itself does not dye mordanted fabrics, the potassium and sodium salts of this colouring matter give on calico mordanted with aluminium and iron pale orange-red and brownish-black shades.

Pure Java kamala contains, according to Flückiger (Arch. Pharm., 1892), 1·363 to 1·488 per cent. of ash, whereas in the kamala examined by Anderson (*loc. cit.*), 3·49 per cent. was present. The best commercial varieties usually contain about 5 per cent. of mineral matter (Seidler and Waage, Ber. Deut. pharm. Ges., 1891, 80); but the inferior qualities are highly adulterated (50—87 per cent.) with sand, earthy impurities, red brick-dust, etc. (Perkin, *loc. cit.*, and J. Soc. Chem. Ind., 1900).

WARAS.

Waras, also called "wars" and "wurrus," consists of a purplish resinous powder which covers the seed pods of *Flemingia congesta* (Roxb.), an erect woody shrub growing in the thickets and forests of the warmer part of India. According to Watt ("Dictionary of Economic Products of India," iii., 482), it is collected also in Africa in the neighbourhood of Harrar, and is sent to Arabia, chiefly to

Yemen and Haddramant, where it is used as a dye, as a cosmetic, and as a specific against colds. According to Wardle, waras is distinctly inferior as a dye to kamala, which it closely resembles, and contains only a small amount of colouring matter compared with the yellow vegetable dyes of commerce. It is suitable as a dye for silk rather than for wool, but is quite useless with cotton. It has been introduced into England from Aden as an adulterant or substitute for kamala (Flückiger and Hanbury's Pharmacographica, 1879, 576). Under the microscope waras appears as orange-brown lumps, frequently circular and closely resembling kamala.

Flemingin, $C_{12}H_{12}O_3$ (provisional), is a dull orange-red crystalline powder consisting of star-shaped groups of minute prismatic needles, which melt at 171—172°, and closely resembles the rottlerin of kamala. Solutions of the alkali hydroxides dissolve it with an orange-brown tint, but these solutions when boiled do not deposit resinous matter, as is the case with rottlerin. On fusion with alkali *salicylic acid* and acetic acid are produced.

Silk suspended in a solution of flemingin in dilute sodium carbonate, and the whole gradually raised to the boiling temperature, is dyed golden yellow, slightly duller than the shade given by rottlerin; but, on the other hand, flemingin possesses much the stronger dyeing power of the two.

In addition to flemingin waras contains a trace of a yellow crystalline colouring matter, *homoflemingin*, melting-point 165—166° (C = 69·97; H = 5·75), together with some quantity of two resinous substances: (*a*) $C_{12}H_{12}O_3$ (?), melting-point 162—167°, and (*b*) $C_{13}H_{14}O_3$ (?), melting below 100°. Fused with alkali these latter gave salicylic and acetic acids, and appear to be allied to flemingin.

Added to a boiling solution of its own weight of sodium carbonate, waras dyes silk golden yellow shades, which are brightened by rinsing in very dilute acetic acid. Contrary to the statement of Wardle, it is to be regarded as a decidedly superior dyestuff to kamala (Perkin, Chem. Soc. Trans., 1898, 73, 659).

SAFFRON.

Saffron consists of the dried petals of the *Crocus sativus* (Linn.), a plant which flowers in September and October, and is distinct from the ordinary spring crocus (*Crocus vernus*, All.). It is a native of the East, but is cultivated in Spain, the South of France, and Austria, and is employed for flavouring purposes, for the staining of articles of diet, and to a very limited extent as a dyestuff. Saffron contains the

aromatic oil known as *saffron oil*, *picrocrocin*, a bitter compound, and *crocin*, or *polychroit*, the glucoside of the colouring matter. Pfyl and Scheitz (Zeit. Nahr. Genussm., 1908, 16, 337) failed, however, to obtain Kayser's "picrocrocin" (Ber., 17, 2228) though using the methods employed by him. These authors state that by extraction of saffron with chloroform they isolated three products: (i) a colourless crystalline substance, melting-point 280° C., which does not reduce Fehling's solution; (ii) a yellow crystalline substance, melting-point 164° C., readily soluble in water or alcohol, which when boiled with acid developed the odour of saffron oil, and gave a sugar, probably lævulose; and (iii) a crystalline hydrocarbon, melting-point 118° C. (cf. Schüler, Diss. Munich, 1899, and Hilger), apparently similar to the hydrocarbon found in marigold petals, arnica flowers, etc. According to these authors, the second substance referred to above somewhat resembles the "picrocrocin" described by Kayser. From alcoholic extraction of saffron the same authors obtained (i) the colouring matter; (ii) a sugar (possibly lævulose); and (iii) a glucoside, which on hydrolysis yields saffron oil and a sugar (possibly lævulose).

Crocin, $C_{44}H_{70}O_{28}$ (?), forms a yellow-brown amorphous powder, readily soluble in water and dilute alcohol, and dissolves in sulphuric acid with a deep blue coloration which, on standing, becomes violet, then red, and finally brown. (Cf. Bixin, Nycanthin, and Carotene.)

When digested with hot dilute hydrochloric or sulphuric acids, crocin is hydrolysed into crocetin and glucose, a reaction which, according to Kayser (*loc. cit.*), proceeds as follows:—

$$2C_{44}H_{70}O_{28} + 7H_2O = C_{24}H_{46}O_9 + 9C_6H_{12}O_6$$

Crocetin consists of a red amorphous powder, readily soluble in alcohol and soluble in alkaline solutions with an orange-red colour. Kayser assigned the formula $C_{24}H_{46}O_9$ to crocetin, but according to Wiess (J. pr. Chem., 101, 65) this is more probably $C_{16}H_{18}O_6$, whilst Schunck and Marchlewski (Annalen, 278, 357) find that Kayser's analytical figures are in agreement with the simpler formula $C_{15}H_{20}O_4$. Decker (Arch. Pharm., 1914, 252, 139) has shown that although crocetin is amorphous it yields crystalline salts with alkalis, and by analysis of these and molecular weight determinations of the acetyl derivative, he concludes that crocetin has the composition $C_{10}H_{14}O_2$.

The sodium or potassium salts are obtained by adding alcoholic sodium, or potassium, hydroxide to a solution of crocetin in dilute aqueous caustic soda, or potash, till no further precipitate is formed,

warming, when the respective precipitates redissolve, and then allowing the solution to cool when the salts separate in a crystalline condition. *Crocetin sodium salt* crystallises in needles; the *potassium salt* in nodular aggregates; the *ammonium salt*, from dilute alcohol, in lustrous red needles. Other salts—aniline, pyridine and quinoline—have also been prepared by Decker.

Acetylcrocetin, $C_{10}H_{12}O_2(CH_3CO)$, crystallises in red needles, melting-point 174° C. It is prepared by heating the potassium salt with acetyl chloride. With lead acetate crocetin gives a deep brown precipitate, and with sulphuric acid a deep blue solution.

When crocetin is brominated in chloroform solution, a *dibromide* is produced which crystallises in yellow octahedra, melting-point 103—104° C., and the production of this is considered by Decker as evidence of the presence of a double bond in the crocetin molecule.

When oxidised with bromine in alkaline solution, crocetin yields a product $C_7H_{10}O_2Br_2$, which forms colourless felted needles.

Dyeing Properties.—Crocetin dyes aluminium and tin mordanted fabrics dull orange and yellow shades respectively.

According to Rochleder, the Chinese dyestuff "Wongsky" (q.v.), which consists of the fruit of the *Gardenia grandiflora* (Lour.), also contains crocin (Jour. Chem. Soc., 1858, 475).

Green Ebony.

Green ebony is a yellow dyewood formerly employed to some extent in this country, but is now almost entirely replaced by other colouring matters. It is a native of Jamaica or West India, and is obtained from the *Excœcaria glandulosa* (Siv.) or *Jacaranda ovalifolia* (R. Br.). The trunk of the tree is about 6 inches in diameter; the wood is very hard, and of an orange-brown colour when freshly cut, and stains the hands yellow. References to this dyestuff are meagre, and it does not appear to have been ever largely employed. Bancroft ("Philosophy of Permanent Colours," 1813, ii., 106) states that green ebony contains a species of colouring matter very similar to that of the *Chlorophora tinctoria* (Gaudich) (Old fustic), and is sometimes employed in its stead; and O. Neill ("Dictionary of Calico Printing and Dyeing," 1862) mentions that it is used in dyeing greens and other compound shades. Until recently it had a limited sale in Yorkshire as a dye for leather, but appears to have entirely passed out of use as a woollen dyestuff. It is now little used in silk dyeing, but was formerly employed for greening blacks.

Green ebony contains two crystalline colouring matters, which are distinguished by the fact that whereas one, excœcarin, is not precipitated by lead acetate solution, the second, jacarandin, is completely deposited by this reagent (Perkin and Briggs, Chem. Soc. Trans., 1902, 81, 210).

Excœcarin, $C_{13}H_{12}O_5$, crystallises in lemon-yellow needles, sparingly soluble in cold alcohol, and melting with effervescence at 219—221°. It is soluble in aqueous and alcoholic alkaline solutions with a violet-red coloration, and these liquids, on exposure to air, are rapidly oxidised, and assume a brown tint.

Excœcarin does not dye mordanted fabrics, but is a substantive dyestuff in that it has a weak but decided affinity for the animal fibres with which it gives, preferably in the presence of tartaric or oxalic acid, yellow shades. *Benzoylexcœcarin*, $C_{13}H_9O_5(C_7H_5O)_3$, consists of colourless needles, melting-point 168—171°, and *excœcarindimethyl ether*, $C_{13}H_{10}O_5(CH_3)_2$, of yellow needles, melting-point 117—119°. On fusion with alkali excœcarin gives *hydroquinonecarboxylic acid* ($CO_2H : OH : OH = 1 : 2 : 5$), and a substance melting at 124°, which is probably *hydrotoluquinone* ($CH_3 : OH : OH = 1 : 2 : 5$).

By the action of bromine upon a solution of excœcarin in alcoholic potassium acetate *excœcarone*, $C_{13}H_{10}O_5$, flat copper-coloured needles or leaflets, melting at about 250°, is produced, and this by the action of sulphurous acid is reconverted into excœcarin. With alcoholic quinone solution excœcarin gives the compound $C_6H_4O_2 . C_{13}H_{12}O_5$, minute green-coloured leaflets, melting with decomposition at 190°, and from this sulphurous acid also regenerates excœcarin. From these results it appears evident that excœcarin contains free hydroquinone hydroxyls.

Jacarandin, $C_{14}H_{12}O_5$, yellow plates or leaflets, melting-point 243—245°, dissolves sparingly in alcohol and the usual solvents to form pale yellow liquids having a green fluorescence. With caustic alkali solutions it gives orange-red liquids; with alcoholic lead acetate a bright orange coloured precipitate; and with alcoholic ferric chloride a dark greenish-black solution. It dyes mordanted woollen fabrics the following shades:—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Dull yellow-brown.	Orange-brown.	Bright golden yellow.	Deep olive.

Acetyljacarandin, $C_{14}H_{10}O_5(C_2H_3O)_2$, pale-yellow needles, melts at 192—194°, and when digested with boiling alcoholic potassium acetate gives the salt $(C_{14}H_{12}O_5 . C_{14}H_{11}O_5)K$, yellow needles.

Benzoyljacarandin, $C_{14}H_{10}O_6(C_7H_6O)_2$, forms yellow prismatic needles, melting-point 167—169°.

As indicated by Bancroft (*loc. cit.*) the colours given by green ebony are similar in character to those yielded by old fustic. Employing mordanted woollen cloth the following shades are produced:—

Chromium.	*Aluminium.*	*Tin.*	*Copper.*	*Iron.*
Dull yellow-brown.	Dull brown-yellow.	Golden yellow.	Pale brown.	Olive-green.

With 40 per cent. of the dyewood the iron mordant gives greener and brighter shades than with larger amounts, in which case a browner colour is produced. Possibly from this green shade, and the extremely hard and compact nature of the wood, the name "green ebony" has originated.

The Colouring Matter of Cotton Seed.

Cotton seeds contain, in addition to cotton-seed oil, a phenolic substance *gossypol*, which remains dissolved in the oil when this is expressed.

By extracting the oil with caustic soda and neutralising the solution thus obtained a voluminous precipitate separates which consists of the colouring matter admixed with fatty acids, and the products of its own oxidation. For the isolation of gossypol Marchlewski (J. pr. Chem., 1899, 60, 84) employed a partially purified preparation of this character from which the main bulk of the fatty acids had been eliminated. By extraction with ether, repeated crystallisation from glacial acetic acid, and from a mixture of alcohol and 50 per cent. acetic acid, it was isolated in the form of small yellow prisms.

As the result of analyses of this substance dried *in vacuo* over sulphuric acid, Marchlewski suggested two formulæ, $C_{13}H_{14}O_4$ and $C_{22}H_{24}O_{10}$, and of these the first is considered preferable. Preparations dried at higher temperatures appeared to suffer alteration as they thus became darker, and had then a lower melting-point.

Thus the gossypol when quickly heated melted at 188°, but when previously dried at 125—130°, at 179—180°. It is easily soluble in the usual organic solvents, and dissolves in sulphuric acid with a cherry-red coloration, a reaction by which its presence in cotton-seed oil can be detected. In alkalis, gossypol dissolves with a yellow coloration which rapidly changes to violet, and then slowly fades. The ready susceptibility of alkaline gossypol solutions to air oxidation accounts largely for the impure nature of the crude colouring

matter isolated by such reagents from the oil, and it appears that if care is taken in the process, it is possible to obtain a much cleaner material in the first instance. An alcoholic solution of gossypol gives with ferric chloride a dark green coloration and with the neutral and basic acetates of lead a deep yellow precipitate. The analysis of the lead salt corresponded to $C_{13}H_{12}O_4Pb$. According to Marchlewski, gossypol yields amorphous acetyl and benzoyl derivatives and appears to possess two hydroxyl groups. It contains no methoxy groups, and is not a glucoside. It dyes iron mordanted material a grey shade, but the product obtained by a careful oxidation of its alkaline solution possesses, it is stated, tinctorial properties of greater importance. Gossypol can be employed on cotton fabrics as a mordant for the basic colouring matters.

F. E. Carruth (Amer. Chem. J., 1918, xi., 4, 647) isolates gossypol from the decorticated cotton-seed kernels which have been crushed by rollers before they are "cooked" in the oil mill. From these a considerable amount of oil is removed by percolation with ligroin, and the residue is then extracted with ether and the extract evaporated. The product is now treated with one-half to one-third its volume of glacial acetic acid, and on keeping for some days, or more quickly by gentle warming, crystals of *gossypol acetate* separate. For purification it is dissolved in ether, glacial acetic acid is added, and the solution evaporated until crystallisation commences.

To obtain gossypol itself an ethereal solution of the acetate is treated with water, and the ether distilled off. The gossypol thus remains suspended in the water as crystalline crusts, and may be recrystallised from alcohol.

A second interesting method consists in adding aniline to an ethereal extract of cotton seed. The solution after warming on the water-bath gradually deposits on standing an orange-yellow microcrystalline precipitate, which apparently consists of an aniline salt of gossypol, $C_{30}H_{28}O_9$, $2C_6H_5NH_2$ or $2C_{30}H_{28}O_9$, $5C_6H_5NH_2$. The yield is practically quantitative, and the process may be used to estimate gossypol in extracts of cotton-seed products.

To regenerate gossypol from the aniline compound, it is dissolved in hot alcoholic potassium hydroxide, and the aniline removed by steam distillation. From the alkaline liquid the gossypol is precipitated on acidification, and may be purified by conversion into the acetate according to the method given above.

Gossypol acetate, a molecular compound of gossypol and acetic acid, is evidently the substance described by Marchlewski as the free colouring matter. It is a comparatively stable substance, and when

heated does not evolve acetic acid readily below 180°. Its formula determined by alkali titration is $C_{30}H_{28}O_9$, $C_2H_4O_2$ or $C_{30}H_{30}O_9$, $C_2H_4O_2$. Hence gossypol itself is $C_{30}H_{28}O_9$ or $C_{30}H_{30}O_9$, and this result is in harmony with other analytical figures given in Farrant's paper.

Gossypol acetonate, $C_{30}H_{28}O_9.CH_2.CO.CH_3$, is obtained as glistening crystals when gossypol is dissolved in acetone, and the solution concentrated. Like the acetate it is a stable compound, and when heated at 140—150° it alters but little in weight.

Acetyl and benzoyl derivatives of gossypol could not be obtained in a crystalline condition, but as a result of their examination the evidence was sufficient to indicate that four or five hydroxyl groups are present in gossypol. When gossypol is heated to 186—190° it fuses with the evolution of vapour, and then solidifies to a black mass. On treating the residue with ether a sparingly soluble yellow crystalline compound *B gossypol* separates, which is much less toxic than gossypol itself, and melts at about 246—248°. Again, by fusion with alkali, a second new crystalline substance *C gossypol* can be obtained, and this, which is soluble in alkalis with a blue colour is probably closely related to the purple oxidation product of gossypol referred to above.

Cotton-seed meal which has been submitted to the "Cooking process" loses much of its toxic property, and contains then practically no gossypol. By extracting this product with aniline, the aniline compound of *D gossypol* which crystallises in orange-yellow prisms can be isolated.

Alcoholic potash converts this compound into *D gossypol* itself, yellow crystals, which darken and soften at about 256°.

From the cooked meal 1·2 per cent. of the aniline compound can be obtained. These products have not as yet been closely examined.

ERIOCOCCUS CORIACEUS.

This is a scale insect occurring in clusters consisting of small pinkish-white sacs, which encases the stems of young shoots of the Eucalypti, more especially those on old or burnt stumps. These insects contain a colouring matter which dyes wool mordanted with chromium, aluminium, tin, and iron, brown, light amber, pale orange-brown and sage-green shades respectively. The colours thus obtained are not specially brilliant, and are not fast to alkalis (Gurney, Report of the Australasian Association for the Advancement of Science, 1898. Section B, 273).

ANNATTO.

This is derived from the fruit of the *Bixa orellana* (Linn.), a shrub found native in Central America, and cultivated in Brazil, Guiana, Mexico, the Antilles, and India.

To prepare the dyestuff, the seeds and pulp are removed from the mature fruit, macerated with water, and the mixture is left to ferment. The product is strained through a sieve, and the colouring matter which settles out is collected, partially evaporated by heat, then placed in boxes, and finally dried in the sun.

Annatto comes into the market in the form of cakes, and among the different varieties Cayenne annatto is the most esteemed, and is considered to be the richest in colouring matter. It should contain from 10 to 12 per cent. of the pure dye, and not more than 5 per cent. of ash, whereas the amount of colouring matter in the Bengal product is frequently lower than 6 per cent.

In 1848 Dumontal devised a new method for the preparation of annatto, in which fermentation is avoided, and the pulp is simply washed out from the capsules and off the seeds. This product known as *bixin* is said to be five to six times more valuable than ordinary annatto (Crookes, "Dyeing and Calico Printing").

The colouring matters of this dyestuff were first investigated by Chevreul ("Leçons de Chimie appliquée à la Teinture"), who isolated two substances, one yellow, which was called *orrellin*, soluble in water, and a second, *bixin*, which is red and very sparingly soluble.

Bixin, the useful colouring matter, was subsequently examined by numerous chemists, who were only successful in preparing it as an amorphous powder, and its isolation in a crystalline condition was first achieved by Etti (Ber., 7, 446; 11, 864).

Etti digested 1·5 kilos. of purified annatto with a solution of 150 grammes of calcined soda ash in 2·5 kilos. of 80 per cent. alcohol on the water-bath at 80°. The mixture was filtered and the residue pressed between warm plates, and again extracted with 1·5 kilos. of warm 60 per cent. alcohol.

The alcoholic filtrate was diluted with half its volume of water, concentrated, sodium carbonate solution added, and the crystalline precipitate of sodium bixin was collected after several days, and pressed. The product purified by solution in 60 per cent. alcohol at 70—80° and reprecipitation with sodium carbonate was finally made into a cream with alcohol, and this, when neutralised with hydrochloric acid, yielded crystalline bixin.

A simpler method has been more recently devised by Zwick (Ber.,

30, 1972). Well-dried annatto is extracted for twenty-four hours with boiling chloroform, the extract evaporated, and the residue thoroughly exhausted with ligroin. The product is crystallised from chloroform, and after washing with ligroin is repeatedly recrystallised from the former solvent.

Bixin, $C_{28}H_{34}O_5$ (Etti, *loc. cit.*; Marchlewski and Matejko, Chem. Zentr., 1906, [ii.], 1265), consists of brown-red or deep-red rhombic crystals, which, when slowly heated, melt at 191·5°, and when rapidly heated at 198°. It is sparingly soluble in the usual solvents, and of these it is most readily dissolved by chloroform or alcohol. Concentrated sulphuric acid dissolves bixin with a cornflower-blue coloration, and this reaction is given by minute traces of the substance (cf. Crocin, p. 603, and Nycanthin, p. 614).

Monosodium bixin, $C_{28}H_{33}O_5Na + 2H_2O$, is best prepared by dissolving 10 grammes of bixin in a solution of 1·2 grammes of sodium carbonate in 300 c.c. of 12 per cent. alcohol at 70° (Etti, Zwick). It is deposited on cooling in dark-red iridescent crystals, and can be obtained in the anhydrous condition by recrystallisation from 70 per cent. alcohol (Marchlewski and Matejko).

Disodium bixin, $C_{28}H_{32}O_5Na_2 + 2H_2O$, is obtained when 20 grammes of bixin is dissolved in a solution of 10 grammes sodium carbonate in 600 c.c. of boiling 12 per cent. alcohol. It consists of a dark-red amorphous powder (Etti). *Monopotassium bixin*, $C_{28}H_{33}O_5K + 2H_2O$, and *dipotassium bixin*, $C_{28}H_{32}O_5K_2 + 2H_2O$, have also been prepared.

Bixin contains one methoxyl group. Distilled with zinc-dust, bixin yields, according to Etti, *metaxylene*, *metaethylxylene*, and a hydrocarbon, $C_{14}H_{14}$, boiling-point 270—280°.

According to Zwick, bixin is readily reduced by sodium amalgam, and a compound, $C_{28}H_{40}O_7$, is thus produced. Marchlewski and Matejko, on the other hand, studied the action of zinc-dust and acetic acid, and obtained in this manner an orange-coloured crystalline substance which possessed a strong metallic lustre. When slowly heated it melts at 200·5°, but if the operation is carried out rapidly, at 208—210°. This compound is evidently of an unstable nature, for whereas when freshly prepared it gives C = 75·4, H = 7·7 per cent., on standing for some days in the air it becomes colourless and then gives C = 58·6, H = 5·8 per cent. At 100° this change occurs more rapidly.

More recently there has been much controversy as to the correct formula for bixin.

Van Hasselt (Chem. Weekblad, 1909, 6, 480) contends that

pure bixin, which melts at 189°, is $C_{20}H_{24}O_5$ rather than $C_{28}H_{34}O_5$, as proposed by Etti (*loc. cit.*). If heated at 190° in a current of hydrogen, 1 gramme mol. of bixin yields 1 gramme mol. of *m*-xylene, and no other volatile product, though it is not to be considered that a *m*-xylene nucleus exists as such in the bixin molecule. No palmitic acid could be obtained from bixin as Zwick suggests. Whereas both Etti and Zwick described mono- and dipotassium salts of bixin, the latter is not in reality a compound of bixin, but of a new substance termed *norbixin*, OK . $C_{23}H_{30}O_3$. OK, produced by a substitution of a methyl of the methoxy group present in the former by potassium (Rec. trav. chim., 1911, 30, 1). Norbixin, $C_{23}H_{32}O_5$, consists of a light red-coloured crystalline powder which decomposes at about 240°, and is distinguished from bixin by its insolubility in chloroform.

Potassium bixinate with methyl sulphate gives *bixin methyl ether*, $B(OMe)_2$, or $C_{30}H_{36}O_5$, plates, melting-point 156° (1909), and the same compound is obtained when a solution of bixin in methyl alcohol is treated with potassium hydroxide and methyl sulphate (1911). On treatment with potassium hydroxide, bixin methyl ether is converted into norbixin. *Bixin ethyl ether*, $C_{31}H_{38}O_5$, violet crystals, melts at 138°, and by methylation forms *norbixin methyl ethyl ether*, OMe . B . OEt, melting-point 149°.

Potassium norbixin, obtained from bixin and alcoholic potash, gives with ethyl sulphate *norbixin diethyl ether*, $C_{23}H_{30}O_3(OEt)_2$, melting-point 121°, together with *norbixin ethyl ether*,

$$C_{23}H_{30}O_3(OEt)\,(OH),$$

melting-point 176°.

The relationship between norbixin, bixin, and bixin methyl ether is shown as follows :—

OH . R . OH OH . R . OMe OMe . R . OMe

According to Hasselt, *iso-bixin methyl ether*, melting-point 149°, is produced when norbixin ethyl ether is methylated, and it is thus evident that the two hydroxyls of norbixin are not symmetrically situated. *Iso-bixin*, OH . R . OMe, melts at 178°, and may be obtained by the partial hydrolysis of bixin methyl ether, and this, by ethylation with ethyl sulphate, gives norbixin diethyl ether, melting-point 121°, the methyl being thus replaced by an ethyl group. Isobixin is distinguished from bixin by the greater stability of its methyl group in presence of potassium hydroxide solution.

The product of the reduction of bixin obtained by Marchlewski

and Matejko, and referred to above, is considered by van Hasselt to consist of *dihydrobixin*, $C_{29}H_{36}O_5$. He has also described *dihydrobixin methyl ether*, $C_{30}H_{38}O_5$, melting-point 174°; *dihydro-iso-bixin*, $C_{29}H_{36}O_5$, melting-point 190°; and *dihydro-norbixin*, $C_{28}H_{34}O_5$, which decomposes at 235°.

By the action of bromine, bixin yields *bixin decabromide*,

$$C_{29}H_{34}O_5Br_{10},$$

whereas bixin methyl ether yields the analogous compound,

$$C_{30}H_{36}O_5Br_{10},$$

and both these substances are colourless amorphous powders. Attempts to benzoylate or acetylate bixin were unsuccessful.

On the other hand, Heiduschka and Riffart (Arch. Pharm., 1911, 240, 43) consider that the old formula $C_{28}H_{34}O_5$ for bixin is preferable to that of $C_{29}H_{34}O_5$, advocated by van Hasselt. Bixin, by the action of bromine in the presence of chloroform, gives the compound $C_{28}H_{34}O_5Br_{10}$, 4HBr, melting at 143°, and this by heating at 100° is converted into the decabromide $C_{28}H_{34}O_5Br_{10}$, which can be obtained crystalline from alcohol, but is unstable. By the action of chlorine on bixin and norbixin respectively, the amorphous compounds $C_{28}H_{34}O_5Cl_{10}$, 4HCl and $C_{27}H_{32}O_5Cl_{10}$, 4HCl can be prepared.

Van Hasselt (Rec. trav. chim., 1914, 33, 192), however, maintains that his formula for bixin, $C_{29}H_{34}O_5$, is correct, and states that the discrepancy shown by the results of his own work and that of Heiduschka and Riffart arises from the fact that bixin is readily susceptible to oxidation with the formation of amorphous products. The bixin of these latter authors was not completely pure, and it is quite correct that specimens which are purified by their method give figures in harmony with the older formula, $C_{28}H_{34}O_5$. Again, the analytical numbers given by Marchlewski and Matejko for hydrobixin are explainable if bixin is given the formula $C_{29}H_{34}O_5$.

A new formula, $C_{25}H_{27}O_3 \cdot OMe$, for bixin was now suggested by Herzig, Faltis, and Mizzan (Monatsh., 1914, 35, 997), who state that it is difficult to correctly analyse bixin unless special precautions are adopted. *Dihydrobixin*, the product of the action of zinc-dust and acetic acid on bixin, melts at 178—179°, whereas the methyl ether obtained by means of diazomethane and bixin, or methyl sulphate and potassium bixin, melts at 158°.

Though, as Hasselt states, bixin at 190—200° yields *m*-xylene, the reaction is hardly of a quantitative nature, in that the crude oil, though containing this hydrocarbon, possesses no constant boiling-

point. Rinkes (Chem. Weekblad) suggests that the formula of bixin is $C_{27}H_{32}O_4$, though Herzig and Faltis (Ber., 1917, 50, 927) in reply, reiterate that the expression $C_{26}H_{30}O_4$ is to be regarded as correct, and that the real difficulty lies in the combustion of this colouring matter. Heiduschka and Panzer (Ber., 1917, 50, 546) point out, however, as the result of further investigation, that the main difficulty is in the purification of the substance. The most satisfactory products are those obtained by means of acetone and ethyl acetate, which, when analysed, give figures agreeing with the formula

$$C_{25}H_{30}O_4$$

When ozonised, methyl bixin forms an *ozonide*, and this by distillation, and partly by the action of calcium carbonate, gives among other products, *methyl β-acetyl acrylate*, and a crystalline compound, $C_8H_{10}O_2$, melting-point 85°, which yields an oxime, melting-point 106°, and may be the methyl ester of a ketonic acid. Methylbixin thus appears to contain the linkage

$$\ddot{C} . Me . CH : CH . \ddot{C} . OMe$$

(Rinkes and Hasselt, Chem. Weekblad, 1916, 13, 244, and 14, 888).

Sodium hyposulphite reduces bixin to *α-hydrobixin*, red needles, melting about 200°, norbixin to *α-hydronorbixin*, violet crystals, and methylbixin to *α-hydromethylbixin*, violet needles, melting-point 190—192°.

On the other hand, with titanium sesquioxide, bixin gives *β-hydrobixin*, norbixin *β-hydronorbixin*, and methylbixin *β-hydromethylbixin*, the latter of which melts at 170°. By the action of zinc-dust both α- and β-hydrobixins are converted into the same *γ-hydrobixin*, yellow crystals, melting-point 207° (van Hasselt, *ibid.*, 1916, 13, 429).

Dyeing Properties.—Annatto is still employed to a fair extent for colouring oils and butter, but is almost extinct as a dyestuff in this country. As the orange-red colour which it yields is extremely fugitive to light, it has at no time been very extensively used. On the other hand, it resists the action of soap and dilute acids very well.

In order to dye cotton, the annatto is first dissolved in a boiling solution of carbonate of soda, and the goods are then entered and left in the bath for a quarter of an hour. They are subsequently pressed out, and washed in slightly acidulated water or alum solution.

For silk, the bath is made up with equal parts of annatto and sodium carbonate ; soap is also usually added, and the dyeing is

continued at 50° for about an hour, according to the shade required. The colour produced can be rendered somewhat more yellow by passing the fabric through a weak solution of tartaric acid.

Wool is dyed at 80—100° without any addition to the bath.

NYCANTHES ARBOR-TRISTIS.

Nycanthes arbor-tristis (Linn.).—This is a large shrub with rough leaves and sweet-scented flowers occurring in the sub-Himalayan and Tarai tracts; also in Central India, Burma, and Ceylon. The flowers open towards evening and fall to the ground on the following morning. The corolla tubes are orange coloured and give a beautiful but fleeting dye, which is mostly used for silk, sometimes in conjunction with "kusum" or turmeric, occasionally with indigo and kath (Watts, "Dict. Econ. Prod. of India," 1891, 5, 434).

According to Hill and Sirkar (Chem. Soc. Trans., 1907, 91, 1501), these flowers yield a red crystalline colouring matter, *nycanthin*. An aqueous decoction treated with 1 per cent. of hydrochloric acid is warmed gently for several hours, the precipitate collected and extracted with boiling alcohol. The extract heated with 1 per cent. hydrochloric acid deposits the colouring matter in red flakes which are washed with alcohol, and crystallised from pyridine or phenylhydrazine.

Nycanthin separates from pyridine in minute regular hexagons, and from phenyl-hydrazine in rhombic crystals; these are yellow while wet, but brick-red when dry, and melt between 234—235°. Perkin (Chem. Soc. Trans., 1912, 101, 1539), however, states that this is incorrect and should be 285—287°. It dissolves in alkalis to form a yellow solution from which it appears to be reprecipitated unchanged by acids, and contains no methoxyl group. With sulphuric acid it gives a most intense blue colour, which, however, rapidly turns yellow, and in this respect resembles bixin, the colouring matter of annatto (*Bixa orellana*, Linn.).

The analyses of Hill and Sirkar (*loc. cit.*) agree closely with $C_{20}H_{27}O_4$ or $C_{15}H_{20}O_3$, but of these formulæ the former was considered preferable.

Acetylnycanthin, $C_{20}H_{26}O_4 . C_2H_3O$, and a bromine compound, both of which are amorphous, have been prepared by these authors. Mannitol was also isolated from the flowers.

For dyeing purposes the material (silk or cotton) is simply steeped in a hot or cold decoction of the flowers. The addition of alum and lime juice to the dye-bath is said to render the colour more permanent.

CEDRELA TOONA.

The *Cedrela toona*, the Toon or Indian mahogany tree, is a large tree 50 to 60 feet, although occasionally reaching 100 feet in height, the wood of which closely resembles mahogany and is imported into England under the name of "Moulmein Cedar" and much used for making furniture. It occurs in the tropical Himalaya from the Indus eastward, throughout the hilly districts of Central and Southern India to Burma, and is also found in Java and Australia. The flowers constitute one of the less important Indian natural dyestuffs, and are reputed to yield both a red and a yellow dye (known in Bengal as "*Gunari*," which is applied without mordants). Although considerably employed for dyeing purposes alone, the flowers are also used in Burma in conjunction with safflower and together with turmeric to produce the sulphur-yellow colour or "basanti" of Cawnpore.

To isolate the colouring matters, Perkin (Chem. Soc. Trans., 1912, 101, 1539) digested an aqueous extract of the flowers with a little hydrochloric acid at 70—80°, which caused the separation of a reddish-brown precipitate. This collected and dried was exhausted with boiling alcohol, and the solution on evaporation deposited a small amount of a red microcrystalline powder. By re-crystallisation from pyridine and removal of an insoluble amorphous impurity, this separated in large orange-coloured leaflets which contained pyridine, and became red and opaque when washed with benzene or alcohol, the pyridine being thus eliminated.

It melted at 285—287° and with cold concentrated sulphuric acid gave a deep indigo blue liquid, resembling in this property bixin, the colouring matter of annatto, *Bixa orellana* (*loc. cit.*). This compound proved to be identical with the red colouring matter *nycanthin* isolated by Hill (*ibid.*, 1907, 91, 1501) from the flowers of the *Nycanthes arbor-tristis* to which the erroneous melting-point 234—235° had been assigned. The amount which is present in the Toon flowers is very small and does not seem to average more than 0·1 per cent. Though there appears to be little doubt that nycanthin and bixin are closely related, the connection between the two compounds cannot be predicted with any reasonable certainty until chemists are in agreement as to the correct formula of bixin, etc. The analyses of Hill and of Perkin indicate that nycanthin contains approximately C = 72·68, H = 7·75, and the simplest formula to which this corresponds is $C_{15}H_{18}O_3$. Among the numerous expressions proposed for bixin is, however, that of van Hasselt (cf.

Annatto), $C_{29}H_{34}O_5$, and should this eventually prove to be correct, then nycanthin is possibly an oxy- or hydroxy-bixin, $C_{29}H_{34}O_6$ (C = 72·8; H = 7·1).

Addition of zinc-dust to the hot orange-yellow coloured alkaline solution of nycanthin causes decolorisation. From this by acidification a colourless or faintly yellow precipitate separates, and this, as is well known, is a property also possessed by bixin.

Cotton on immersion in a boiling dilute solution of nycanthin in sodium carbonate and subsequently rinsing with acidified water, is dyed an orange shade indistinguishable from that given in these circumstances by annatto, a fact which again points to a relationship between the two colouring matters.

The flowers of the *Cedrela toona* contain in addition to nycanthin a fair amount of *quercetin*, probably as glucoside, and also a second flavone or flavonol dyestuff, the identity of which was not ascertained. A sugar, $C_{12}H_{22}O_{11}$, is also present, and this after purification melted at 165—168°.

Cotton and woollen fabrics can be dyed a dull yellow colour by mere immersion in a boiling extract of Toon flowers. This, however, is not permanent and is removed, although much more quickly from cotton than wool, by the action of soap or dilute alkali. Better results are obtained by the employment of mordants, and the following shades were obtained with mordanted woollen cloth :—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Dull brownish-yellow.	Full golden-yellow.	Bright yellow.	Dull olive-brown.

During these operations, nycanthin or its glucoside apparently plays no part, and the colours obtained are due to the flavone glucosides present. Not only the flowers but the seeds of the *Cedrela toona* are stated to give a red dye.

ALGARROBIN.

A new natural dye product, termed "Algarrobin," obtained from the wood of the carob tree, *Ceratonia siliqua*, found in the Argentine, has recently been placed on the market. According to a report of the United States Consul-General at Buenos Ayres, it is largely employed in the Argentine for dyeing khaki cloth for military purposes, and some quantity is also being imported to the Continent of Europe. It is said to dye the textile fibres a light brown colour, though if these be previously mordanted, more varied shades may be obtained. As it acts also as a mordant for the Coal Tar colours, it

would appear to be a tannin, and may indeed be allied to ellagitannin, as its name suggests (cf. Algarobilla, *loc. cit.*).

Lycoperdon gemmatum.

According to Kotake and Naito (Zeitsch. physiol. Chem., 1914, 90, 254) the fungus *Lycoperdon gemmatum* on extraction with alcohol gives a crystalline brown dyestuff. This is a glucoside, and when hydrolysed gives dextrose and *gemmatein*, $C_{17}H_{12}O_7$, brown needles. Fusion with alkali gives *p-hydroxyphenylacetic acid*, and when oxidised with hydrogen peroxide *homogentisic anhydride* is produced.

Phoenin and Phoenicein.

Phoenin, $C_{14}H_{16}O_7$, the glucoside of the leuco compound of phoenicein, is found in the bark parenchyma cells of the *Copaifera bracteata* (Benth.), (purple wood), and crystallises from water in minute colourless needles or rods, which, on standing in air, develop a faintly violet tint. By boiling with methyl alcohol and hydrochloric acid, phoenin is converted into *phoenicein*, and, on addition of water to the acid solution, is deposited as a red powder, soluble in ammonia, with a violet-blue coloration. Purple wood yields approximately 2 per cent. of phoenicein.

Lokao.

Lokao, a green dyestuff of Chinese origin, is, or rather was, since it has been supplanted by artificial colouring matters, met with in commerce in the form of thin laminæ of a dark bluish or bluish-green colour. Though formerly employed to some extent in Europe, it does not appear, owing to its extremely expensive nature, to have been extensively used. According to Crookes ("Dyeing and Calico Printing," 429), lokao contains from 21·5 to 33 per cent. of ash, 9·3 per cent. of water, and 61·7 per cent. of colouring matter. It is insoluble in water and the usual solvents, but dissolves in sulphuric acid with a red-brown coloration, and also in alkalis, the solution thus obtained gradually acquiring a brown tint.

According to Hellot (Crookes, *loc. cit.*) and others, lokao requires for its preparation two distinct plants, the *Rhamnus dahurica* (Pall.) (hong. pi. lo. chou) and the *R. tinctoria* (Walldst. and Kit.) (pé. pi. lo. chou), the first of which is said to yield a deep and fast colour, whilst from the latter a weak but brilliant colour can be obtained. According to Rüpe ("Die Chemie der natürlichen Farbstoffe," 1900), the plant bark is extracted with hot water, the extract allowed to stand over-night, filtered, and then treated with potassium carbonate

or milk of lime. Cotton yarn is immersed in this mixture, subsequently withdrawn and spread out in meadows over-night and a portion of the daytime, and the operation repeated ten or twenty times. The colouring matter is removed by rubbing the yarn with the hands under cold water, and the precipitate, which settles to the bottom of the receptacle, is washed by decantation, spread on paper and dried in the shade (cf. also Crookes, *loc. cit.*).

According to Cloëz and Guignet (Jahres., 1872, 1068) lokao or Chinese green is, in reality, a lake, and by treatment with ammonium carbonate is converted into the ammonium salt of the colouring matter *lokain*, $NH_4 . C_{28}H_{32}O_{17}$. By the action of dilute sulphuric acid lokain is hydrolysed with formation of *lokaetin*, $C_{18}H_{16}O_{10}$, glucose, and a soluble compound which is precipitated by basic lead acetate.

Kayser (Ber., 1885, 18, 3417) extracted finely powdered Chinese green with concentrated ammonium carbonate solution, added alcohol to the clear liquid, and thus obtained a precipitate of the crude ammonium salt of the colouring matter which he termed *lokaonic acid*. This was collected, extracted with ammonium carbonate, the solution precipitated by alcohol, and the operation repeated several times, the product being finally dissolved in water and the liquid evaporated to crystallisation with the addition of a little ammonia. Thus prepared the *diammonium salt* of lokaonic acid, $C_{42}H_{46}O_{27}(NH_4)_2$, consists of small crystals possessing a bronzy lustre, which at 40° C. commences to lose ammonia, and at 100° gives the *mono-ammonium salt*,

$$C_{42}H_{47}O_{27}(NH_4)$$

The *potassium salt*, $C_{42}H_{46}O_{27}K_2$, separates in the form of a blue amorphous powder, when a concentrated aqueous solution of the diammonium salt is treated with alcoholic potash; whereas the barium salt, $C_{42}H_{46}O_{27}Ba$, obtained by means of barium chloride, has a similar appearance, and the lead salt, $C_{42}H_{46}O_{27}Pb$, is a dark brown powder.

Lokaonic acid, $C_{42}H_{48}O_{27}$, prepared by the decomposition of the diammonium salt with oxalic acid, consists of a bluish-black powder, which, when rubbed, develops a metallic lustre. It is insoluble in the usual solvents, but dissolves in solution of the alkaline hydroxides and ammonia with a pure blue tint.

Treatment with sulphuretted hydrogen changes this to a blood-red colour, which passes to green on exposing the liquid to air. Digested with dilute sulphuric acid on the water-bath lokaonic acid is hydrolysed with formation of lokanic acid and a sugar lokaose.

Lokanic acid, $C_{36}H_{36}O_{21}$, is a violet-black crystalline powder insoluble in water, alcohol, ether, and chloroform, but soluble in alkaline solutions with a violet-blue coloration.

The *ammonium salt*, $C_{36}H_{35}O_{21}NH_4$, the *barium salt*, $C_{36}H_{34}O_{21}Ba$, and the *lead salt*, $C_{36}H_{34}O_{21}Pb$, are described by Kayser.

Hot 50 per cent. potassium hydroxide solution converts lokanic acid into *phloroglucinol* and *delokanic acid*, $C_{15}H_9O_6$, which consists of a brown powder dissolved by dilute alkalis, whereas nitric acid gives with lokanic acid nitrophloroglucinol.

Lokaose, $C_6H_{12}O_6$, obtained by the hydrolysis of lokaonic acid, crystallises in colourless needles, and is optically inactive.

These results have, in the main, been confirmed by the recent work of Rüdiger (Arch. Pharm., 1914, 252, 165), who, however, gives the following compositions to the various products, viz.: *Lokaonic acid*, $C_{42}H_{46}O_{25}$; *Lokanic acid*, $C_{36}H_{36}O_{21}$; *Delokanic acid*, $C_{12}H_8O_6$, and has shown that the sugar "lokaose," obtained by Kayser, has the composition $C_6H_{12}O_5$, not $C_6H_{12}O_6$, and is rhamnose.

By the action of nitric acid (specific gravity 1·4) on delokanic acid (which, like lokanic acid, contains one methoxy group) Rüdiger obtained oxalic acid and a substance that crystallised in orange-yellow needles, melting-point 129°, of the composition $C_8H_7O_5N$, which he considers may be *2-nitro-5-methoxy-benzoic acid* (melting-point 132° C.). The following represents the above-mentioned changes:—

Lokaonic acid { Kayser, $C_{42}H_{48}O_{27}$. / Rüdiger, $C_{42}H_{46}O_{25}$.

H_2SO_4 ↓

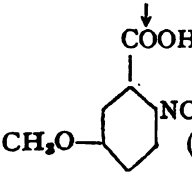
Lokanic acid { K. : $C_{36}H_{36}O_{21}$ + "lokaose" ($C_6H_{12}O_6$). / R. : $C_{36}H_{36}O_{21}$ + rhamnose ($C_6H_{12}O_5$).

$\xrightarrow{HNO_3\ (hot)}$ nitro-phloroglucinol (melting-point 203—204°).

KOH ↓

Delokanic acid { K. : $C_{15}H_9O_5$ / R. : $C_{12}H_8O_6$ } + phloroglucinol ($C_6H_6O_3$).

↓



(?) + oxalic acid.

The composition given to lokaonic acid by Rüdiger is obviously more in keeping with the fact that the process whereby lokanic acid is obtained from it is one of hydrolysis, and Kayser's figures do not represent this.

According to Persoz, cotton can be dyed in a weak alkaline solution of lokao, and it behaves also as a vat dyestuff, for which purpose it may be reduced by faintly acid or alkaline stannous chloride. The colour thus obtained is blue, and can be converted into green by the subsequent employment of a yellow dyestuff.

In order to dye cotton a green with lokao, Persoz recommends a bath prepared by adding the pigment to a solution of soap, whereas for silk Michel obtained excellent results by employing lokao and alum solution in the presence of lime salts. For the Chinese and other methods of employing this dyestuff, see Crookes (*loc. cit.*) and Rüpe (*loc. cit.*).

DATISCA CANNABINA (Linn.).

This is a tall, erect herb, resembling hemp, belonging to the *Datisceæ*, and met with in the temperate and sub-tropical Western Himalayas from Kashmir to Nepal. The root, known as *Akalbir*, has been extensively used in Kashmir and throughout the Himalayas as a yellow dyestuff chiefly on alum-mordanted silk; but the colouring matter appears to be present in the whole plant, for the leaves and twigs can also be employed for the same purpose.

The leaves of the *Datisca cannabina* were first examined by Braconnot (Ann. Chim. Phys., [2], iii., 277), who isolated from them a crystalline substance which he named datiscin. Somewhat later it was shown by Stenhouse (Annalen, 1856, 98, 167) that this compound is a glucoside, and when hydrolysed is converted into a sugar, together with a yellow colouring matter, *datiscetin*, $C_{15}H_{10}O_6$.

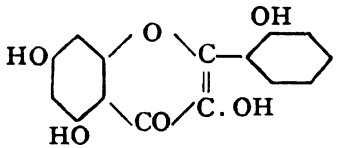
Schunck and Marchlewski (Annalen, 278, 261), however, considered that the formula $C_{15}H_{12}O_6$ was preferable, and showed that, on fusion with alkali, datiscetin gives *salicylic acid*. By the action of dilute nitric acid, a *nitro-salicylic acid* was produced, whereas with strong nitric acid, picric acid, as already indicated by Stenhouse, was formed. Datiscetin appeared to contain methoxyl groups, and was at that time considered by the authors to be most probably a xanthone derivative.

Korczynski and Marchlewski (Ann. d. Akad. Krakau, 1906, 95) have shown that pure datiscetin, $C_{15}H_{10}O_6$, however, does not contain methoxy-groups. It consists of yellow needles, melting-point 268—269°, soluble in alkaline solutions, with a yellow colour, and

gives, with sulphuric acid, a yellow liquid possessing a green fluorescence. When boiled with strong alkaline solutions, phenol and salicylic acid are produced.

Tetraacetyldatiscetin, $C_{15}H_6O_6(C_2H_3O)_4$, forms colourless needles, and melts at 138°; and *tetrabenzoyldatiscetin*, $C_{15}H_6O_6(C_7H_5O)_4$, gives colourless needles, melting-point 190—191°.

Leskiewicz and Marchlewski (Ber., 1914, 47, 1599) by the action of bromine on datiscetin in boiling acetic acid solution obtained *tribromphloroglucinol*, and as a result suggest that this colouring matter is the 1 : 3 : 1′ trihydroxy-flavonol—



Datiscin, $C_{21}H_{24}O_{11}$ (S. and M.), the glucoside, crystallises in silky needles, which melt at about 190°, and dissolve in alkaline solutions with a yellow colour. Hydrolysis with dilute sulphuric acid yields datiscetin and *rhamnose*, not datiscetin and glucose, as stated by Stenhouse (*loc. cit.*).

The dyeing properties of datisca root on wool are very similar to those of old fustic. It is, however, slightly inferior in dyeing power. On cotton it dyes more like quercitron bark, in so far that the olives obtained on iron mordant are bluer in shade, as though some tannin matter were present. It appears to have about the same colouring power as quercitron bark, but gives a brighter yellow with aluminium mordant. Applied to wool, it differs from quercitron bark by giving with chromium mordant an olive-yellow, which is not of such a reddish tinge, and with tin mordant a bright yellow instead of an orange. It is an excellent dyestuff, and worthy to rank with the natural yellow mordant colouring matters at present in use (Hummel and Perkin, J. Soc. Chem. Ind., 1895, 14, 458).

GARDENIA GRANDIFLORA.

The fruit of the *Gardenia grandiflora*, known as "Wongsky," is or was employed in China for dyeing yellow, as an assistant for the production of green colours, and in conjuction with safflower. According to Crookes ("Dyeing and Calico Printing," 422) it has not been much used in this country, and the yellow and orange colours it yields are of a somewhat fugitive character.

Rochleder and Mayer (J. pr. Chem., 74, 1) isolated from it

pectin, the rubichloric acid (chlorogenin) which is present in Madder, Chayroot and Morinda root (*loc. cit.*), tannin, and a red amorphous colouring matter apparently identical with the crocin of saffron (*Crocus sativus*). Persoz obtained the colouring matter as a reddish crystalline mass (Crookes, *loc. cit.*), and found that this dyed cotton when mordanted with alumina, yellow, and when mordanted with iron an olive colour.

In Bancroft's "Philosophy of Permanent Colours," i., p. 285, mention is made of the use of the *Gardenia florida* by the Chinese for the dyeing of scarlet under the name of "unki".

The Decamalee or Dikamali gum, which is obtained in India from the *Gardenia lucida*, contains, according to Stenhouse and Groves (Annalen, 200, 311), *Gardenin*, $C_{14}H_{12}O_6$, melting-point 163—164°, and this was isolated as deep yellow crystals insoluble in water and alkaline solutions.

CHAPTER XIX.

LAKES FROM VEGETABLE COLOURING MATTERS.*

UNTIL the advent of the synthetic dyestuffs, the natural dyestuffs formed the only source of the manufacture of organic pigments (lakes), and though their importance for this purpose has been reduced to a minimum, some of these are, or were until recently, employed for the production of lakes for certain special purposes. A general account of the more important of these older lakes is given here, chiefly as a matter of historical interest, for there can be little doubt that all, or at least most of these will eventually become obsolete.

According to Pliny, the dried scum collected by the dyers of Tyrian purple from their dye liquors furnished a costly purple-coloured pigment employed by painters. The indicum of the Roman artists was probably obtained in the same manner from a woad or indigo vat. Caneparius, a Venetian writer on dyeing in 1619, states that it was the custom of dyers to evaporate the waste lac dye liquors in order to obtain an artificial lac used by artists.

Similar pigments were afterwards prepared or collected from the waste dye liquors of kermes, brazilwood, etc. Such pigments were called by the Italians *laccae*, and these were distinguished from each other by adding the name of the substance whence the colour was derived, e.g. *lacca di verrino* (brazilwood), *lacca di grana* (kermes), *lacca di cremise*, etc.

As to the word lake itself, the Indian "lac" or "lakh" means a hundred thousand, and refers to the immense numbers in which the lac insects (*Coccus laccae*) appear at certain seasons on the branches infested by them.

At the present time true lakes are like those of the early days, being, as is well known, insoluble metallic compounds of organic colouring matters.

Madder-lake.—In the preparation of madder-lake extraction of the madder with *boiling* water was avoided, in order not to dissolve those impurities which would cause the production of a less brilliant lake. It was usual, first of all, to decompose the glucoside of the

* In this chapter is embodied much of an article by the late J. J. Hummel in Thorpe's "Dictionary of Applied Chemistry".

madder, and thus increase the actual colouring matter, by a steeping in slightly tepid water and allowing the mixture to ferment for twenty-four hours, then to wash with cold water and extract with alum solution at 60—70°, employing about equal weights of madder and alum. The hot filtered alum solution of the colouring matter was precipitated as an alumina lake by adding sodium carbonate, and the precipitate was washed.

Another method was to precipitate impurities from a hot filtered decoction of madder by adding a small quantity of lead acetate, then filter, add a solution of alum, and precipitate with sodium carbonate.

Matters could be so arranged as to precipitate basic aluminium sulphate instead of aluminium hydroxide, namely, by adding an insufficiency of sodium carbonate to the cooled solution of alum and colouring matter, and then boil the mixture.

Garancine was preferable to madder for preparing madder-lake, since it does not contain any of the colouring matter in the form of glucoside (ruberythric acid), and the soluble impurities have also been for the most part removed. Thus 1 kilo. garancine was repeatedly extracted for several hours with 20 litres of boiling water containing 0·25—0·5 kilo. alum, and the solution filtered hot through flannel. On cooling, the colouring matter separated from the filtrate as a flocculent precipitate. This was collected and dissolved in ammonia, and the filtered solution precipitated with alum, or stannous chloride, or a mixture of both. The colour intensity of the lake varied with the proportions of ammonia and precipitant employed. A method similar to that described for madder could also be employed in preparing madder-lake from garancine.

Bright carmine-red lakes could be obtained if, in the preparation of madder-lake, an ammoniacal solution of cochineal-carmine was employed for precipitating the alum solution, instead of the sodium carbonate. This method was adopted to render the lower qualities of madder-lakes more attractive. Cheap qualities of madder-lakes were also prepared sometimes by extracting mixtures of madder and Brazilwood with sodium carbonate, and precipitating with alum or a solution of tin.

So-called "crystallised madder-lakes" were such as contained a certain quantity of potassium or sodium sulphate, etc.

"Madder-pink-lake" was simply madder-lake diluted with about seven parts of "blanc fixe" (precipitated barium sulphate).

Madder-lake is entirely, or for the most part, soluble in caustic potash and soda. If chalk or other diluent was present, this remains undissolved. Boiled with dilute sulphuric or hydrochloric acid, the

lake is decomposed, the colouring matter being liberated in the form of a flocculent or crystalline precipitate. In dilute ammonia, pure well-made madder-lake is not soluble (distinguishing test from cochineal-carmine). Up to within a few years ago, a rose-coloured lake was still being prepared from the madder preparation known as "Kopp's purpurine" (*loc. cit.*), and was considered to possess certain characteristics as a paint, which up till then had not been found in other materials.

References.—Colomb, Bull. Mülh., 12, 307; Dingl. poly. J., 73, 47; Persoz, Traité de l'Impression des Tissus, 1, 507; Merimé, *ibid.*, 1, 505; Robiquet and Colin, *ibid.*, 1, 505; Khittel, Polyt. Zentr., 1859, 81.

Cochineal-carmine.—In the preparation of this brilliant scarlet lake, cochineal is extracted in tin-lined vessels with a large quantity of boiling water. Certain additions are made to the filtered decoction, and it is then allowed to stand for several weeks, or even months, in shallow vessels of tin or porcelain, during which period the carmine gradually separates in the form of a fine red powder. The additions referred to have varied with different makers, and include the following: potassium binoxalate, acid potassium tartrate (cream of tartar), alum with or without cream of tartar, hydrochloric acid, etc. In all cases the presence of iron must be strictly avoided. The necessary ingredients may also be added to the water with which the cochineal is boiled, in which case the decoction must be filtered hot, since it rapidly becomes turbid on cooling. The addition of gypsum, calcium carbonate, zinc oxide, etc., so usual in other cases, must be avoided, since these render the lake violet.

The manufacture of cochineal-carmine is now very restricted, and the methods employed for producing the finest product have always been kept secret.

According to Alyon and Langlois, 500 grams cochineal are boiled for one and a half hours in 30 litres water containing 25 grams sodium carbonate. The decanted solution is well stirred up with 25—35 grams powdered alum, and then allowed to settle about twenty minutes; the clear liquid is poured off, a dilute solution of isinglass or albumen is added, and the whole is heated until the carmine collects together in the form of a coagulum. After cooling and allowing to settle, the supernatant liquid is decanted off, the carmine is collected on a filter, washed, and dried at a low temperature. The deeply coloured filtrate serves for the production of carmine-lake.

Even alum alone could apparently be used as the precipitating

agent, according to an old recipe, but it seems likely that in this case water possessing an alkaline reaction must of necessity have been employed. Boil sixteen parts ground cochineal for ten minutes with about 600 parts of water, then add 1 part ground alum, boil a few minutes longer, filter the hot solution, and allow the filtrate to stand in shallow porcelain basins. In the course of a few days the carmine is said to separate in the form of a red slimy precipitate, which is collected and dried. The decanted liquor on standing yields a further quantity of carmine of a lower quality; its precipitation is facilitated by the addition of a small quantity of stannous chloride.

The residual cochineal which has thus been only partially exhausted serves for the preparation of carmine-lake.

In other similar recipes a mixture of alum and cream of tartar is used instead of alum only, but in that of Madame Cenette, at one time a celebrated maker of carmine, the statement that the effective precipitating agents are potassium nitrate and potassium binoxalate, is difficult to understand.

Chinese carmine is said to be prepared by extracting cochineal with a boiling solution of alum, heating the filtered decoction with the addition of a solution of tin in nitric and hydrochloric acid (*aqua regia*), and finally leaving the liquid to stand till the carmine separates.

Cochineal-carmine is insoluble in water, but soluble in alcohol. In ammonia solution it dissolves readily with a purplish-crimson colour; from this solution tartaric acid precipitates the original carmine, for although when dried the precipitate has a brownish-red colour, it becomes bright red when powdered. The following analysis of cochineal-carmine is given by C. Liebermann (Ber., 18, 1969):—

Moisture	17 per cent.
Nitrogenous matter . . .	20 „
Ash	7 „
Colouring matter . . .	56 „
Wax	traces

The ash consists of SnO_2 0·67 per cent., Al_2O_3 43·09, CaO 44·85, MgO 1·02, Na_2O 3·23, K_2O 3·56, P_2O_5 3·20. From these analyses Liebermann considers cochineal-carmine to be a peculiar aluminium calcium protein compound of the carmine colouring matter, somewhat analogous to the Turkey-red lake, in which alizarin is combined with aluminium and calcium. According to the ex-

periments of the late J. Bedford of Leeds, cochineal-carmine can only be prepared if a calcareous water is employed, or if calcium salts are added during the reaction. Cochineal-carmine can, indeed, be readily produced by adding to a cold extract of the dye prepared with a hard water potassium carbonate, alum, and subsequently cream of tartar (or potassium binoxolate) in definite proportion. The carmine precipitate separates very gradually during some days, and has an extremely brilliant character. If a small quantity of stannic chloride is also added to the mixture the precipitation is hastened and the product possesses a more scarlet tint (Perkin, private communication).

Carmine-lake is simply an ordinary aluminium or tin lake of the colouring matter of cochineal, produced by adding sodium carbonate to a cochineal decoction containing alum or stannous chloride, or both.

Florentine-lake is, or was, merely a special quality of carmine-lake, containing usually an excess of alumina, and sold in the form of "drops"; and the so-called Venetian-lake, Hamburg-, Chinese-, Roman-, and Scarlet lakes were all varieties of Florentine-lake.

Brazil Indian-lake or *Lac-lake*, a dark purplish-red lake analogous to carmine-lake, can be prepared in a similar manner from the Indian product lac dye.

Brazilwood-lake was prepared by extracting Brazilwood or peachwood with boiling water, adding alum and tin solution to the filtered decoction, and finally precipitating with sodium carbonate, avoiding excess. Another method was to add precipitated and washed aluminium hydroxide to a filtered decoction of Brazilwood. Freshly prepared decoctions are never suitable for the manufacture of these lakes; they should always be oxidised, by exposure to air or otherwise, in order to change the principle brazilin into the necessary colouring matter brazileïn.

Vienna-lake was a species of Brazilwood-lake, prepared in the following manner: A mixture of ground starch (30 kilos.), chalk (10 kilos.), and a little gypsum, is stirred up with a decoction of Brazilwood; then ground alum (1 kilo.) is added and the whole is well stirred for twelve hours and finally allowed to settle. After decanting the clear liquor, Brazilwood decoction is again added to the residual precipitate, together with a further quantity of alum (1 kilo.), and the stirring is continued as before. This process is repeated until the precipitate has taken up sufficient colouring matter and acquired the character of a lake. The decanted liquors are agitated with fresh starch, chalk, etc., in order to yield further quantities of lake.

In the foregoing process the alum is decomposed by the chalk, and the alumina precipitate thus produced combines with the colouring matter. At first the lakes appear violet through the presence of excess of chalk, but with the continued addition of alum they gradually acquire a crimson colour.

Fine dark carmine-red lakes can be obtained by adding stannous chloride and cream of tartar to a concentrated old decoction of Brazilwood.

YELLOWS.

Persian-berry lake is prepared by extracting Persian berries two or three times with boiling water, dissolving alum in the combined and filtered liquors, and then precipitating with sodium carbonate, taking care to avoid excess. The precipitate is collected on a filter, washed, and sold in the form of paste. This lake, containing much starch, and sold in the dry form, is said to be employed in the colouring of sweetmeats.

Persian-berry carmine is produced if stannous chloride is employed instead of alum in the above process. It is a bright orange-lake employed by calico-printers.

Persian-berry lakes may also be made after the manner of Vienna lake, i.e. with the use of chalk, alum, and starch.

It is essential to employ only freshly prepared decoctions if bright coloured lakes are desired.

Quercitron-yellow lake, *Flavin-lake*, or *Dutch pink* can be made according to the method adopted in the case of Venetian lake, by precipitating a decoction of quercitron bark containing alum with chalk. The methods employed in making yellow lakes from Persian berries may also be used. To ensure bright colours the decoction of quercitron bark is clarified by adding a little gelatin solution, thereby removing the tannic acid. Sometimes milk of lime is used instead, taking care to avoid excess.

It is said that these quercitron colours retained their intensity by gaslight better than all other vegetable yellows, and were thus of value for theatre decorations, etc.

The yellow natural colouring matters, especially flavine and Persian berries, are still in some demand for the production of green lakes by combination with basic green artificial colouring matters.

The yellow lake is first prepared and a solution of the coal-tar colour precipitated upon it by tannin and tartar emetic. A partial

precipitation of the basic colour is effected by the tannic acid in the vegetable colour, but must be completed by a further addition. These lakes are used for wall-papers and for colouring toys.

Stil de Grain was a low quality of Dutch pink, and *English* and *Italian pinks* other qualities of quercitron bark yellow lakes.

APPENDIX.

LIST OF NATURAL DYESTUFFS.

A List of Indian Natural Dyestuffs, compiled from the Preliminary List of Specimens of Products in the Indian Section, Imperial Institute, London, 1900.

Plant.	Commercial Name.	Part Employed.	Colour Produced.
Acacia arabica	Indian gum-arabic tree	Leaves, bark, and pods	Black to dark brown
Acacia catechu	Cutch	—	Red and brown
Acacia concinna	—	Bark	Brown
Acacia farnesiana	Cassie flower	,,	Black
Acacia intsia	—	,,	—
Acacia leucophlæa	—	Bark and leaves	Red
Adhatoda vasica	—	Leaves	Yellow
Aegle marmelos	Bæl fruit	Fruit rind	,,
Albizzia odoratissima	—	Bark	Brown
Aleurites moluccana	Indian walnut	Root	,,
Alnus nepalensis	Nepal alder	Bark	—
Andropogon sorghum	Chinese sugar cane	Seeds	Red
Anogeissus latifolia	—	Leaves	Black
Anona reticulata	Custard apple	Fruit	,,
Aporosa villosa	—	Bark	Red
Areca catechu	Betel-nut palm	Nut	—
Artocarpus integrifolia	Jack fruit tree	Wood	Yellow
Artocarpus lakoocha	—	Roots	,,
Baccaurea sapida	—	Leaves and bark	Green
Bassia latifolia	Butter tree	Bark	—
Bauhinia variegata	—	,,	—
Berberis nepalensis	Nepal barberry	Root	Yellow
Bixa orellana	Annatto	Seeds	Orange and red
Butea frondosa	Bengal kino	Flowers	Yellow
Butea superba	—	Root	Red
Cæsalpinia sappan	Sappan wood	Wood	,,
Careya arborea	—	Bark	—
Carthamus tinctorius	Safflower	Flowers	Red
Cassia auriculata	Tanner's cassia	,,	Yellow
Cassia fistula	—	Bark	Red
Cassia tora	Fœtid cassia	Seeds	Blue and red
Casuarina equisetifolia	—	Bark	Brown
Cedrela toona	Indian mahogany or Toon	Leaves, Flowers	Red and yellow
Ceriops candolleana	Mangrove	Bark	Red and brown
Chloroxylon swietenia	Indian satin wood	,,	Yellow

Plant.	Commercial Name.	Part Employed.	Colour Produced.
Coccus cacti	Cochineal	Insect	Scarlet
Coccus lacca	Lac insect	—	Red
Cordia myxa	Sebesten tree	Leaves	—
Coriaria nepalensis	—	Bark	—
Crocus sativus	Saffron	Flowers	Yellow
Curcuma longa	Turmeric	Root	,,
Cynometra ramiflora	—	,,	Purple
Datisca cannabina	—	,,	Yellow
Delphinium zalil	Asbarg	Flowers	,,
Diospyros embryopteris	—	Fruit	Brown
Erythrina indica	Indian coral tree	Bark	Red
Eugenia jambolana	Black plum	,,	,,
Fibraurea trotteri	—	Root	Yellow
Ficus religiosa	Peepul tree	Bark and leaves	Red-brown
Flemingia congesta	Waras	—	Yellow
Galium rotundifolium	—	Roots	—
Garcinia pedunculata	—	Fruit	—
Garcinia xanthochymus	—	Bark	Yellow
Garuga pinnata	—	Leaves	Red
Geranium nepalense	—	Roots	,,
Gossypium herbaceum	Cotton	Flowers	Yellow
Heritiera fomes	—	Bark	—
Hymenodictyon excelsum	—	Leaves	—
Indigofera tinctoria	Indigo	—	Blue
Indigofera sumatrana	,,	—	,,
Jasminum humile	Jasmine	Root	Yellow
Kandelia rheedii	—	Bark	Red and brown
Lagerstroemia parviflora	—	,,	Black
Lawsonia alba	Henna	Leaves and root	Red
Mallotus philippinensis	Kamela	—	Orange
Mangifera indica	Mango	Bark	Yellow
Melastoma malabathricum	Indian rhododendron	Fruit	Purple
Memecylon edule	Iron wood	Leaves and flowers	Yellow
Mesua ferrea	—	Flowers and bark	—
Mimusops elengi	—	Bark	Brown
Mimusops littoralis	—	,,	,,
Morinda angustifolia	—	Root	Yellow
Morinda citrifolia	Indian mulberry	Root and bark	Red
Morinda exserta	—	Wood, bark, and root	—
Morinda tinctoria	—	Bark	Red
Morinda umbellata	—	Root	Yellow
Moringa pterygosperma	Horse-radish tree	Wood	Blue
Myrica nagi	Box myrtle	—	Pink
Nyctanthes arbor-tristis	—	Flowers	Yellow
Odina wodier	—	Bark	Golden and pale brown
Oldenlandia umbellata	Chay root	Root	Red
Phyllanthus emblica	Emblic myrobalan	Bark and fruits	Black, grey, and brown
Pinus excelsa	Indian pine	Bark	Yellow to deep orange
Pinus longifolia	Long-leaved pine	,,	Yellow

Plant.	Commercial Name.	Part Employed.	Colour Produced.
Pterocarpus marsupium	Indian kino tree	Bark	Red-fawn
Pterocarpus santalinus	Sanderswood	Wood	Red
Rhizophora mucronata	Mangrove	Bark	Chocolate
Rubia cordifolia	Indian madder	Roots	Scarlet
Rubia khasiana	—	,,	,,
Rubia sikkimensis	—	,,	,,
Sarcochlamys pulcherrima	Asoka tree	Leavesandtwigs	Brown
Semecarpus anacardium	Marking nut tree	Fruit and bark	Black
Shorea robusta	Sal tree	Bark	Red and black
Symplocos racemosa	Lodh tree	Twigs, wood, and leaves	Yellow
Symplocos spicata	—	Leaves	,,
Tectona grandis	Teak tree	,,	,,
Terminalia belerica	—	Fruit	Yellow-brown
Terminalia chebula	—	,,	,,
Terminalia tomentosa	Asna or Saj tree	Bark and fruit	Brown
Ventilago madraspatana	—	Bark, roots	Red, purple and chocolate
Woodfordia floribunda	—	Flowers	Pink to red
Xylia dolabriformis	Ironwood tree of Pegu and Arracan	Chips	—
Zizyphus jujuba	Indian jujube	Leaves	Red-pink

Natural Dyes of the Philippines.*

Annatto.
Old Fustic.
Indigo (*I. tinctoria*, L., and *I. suffruticosa*, Mill. = *I. anil*, L.).
Brazilwood (*Cæsalpinia sappan*).
Mahonia nepalensis, D.C., contains berberine.
Turmeric.
Acacia farnesiana, Willd. (Cassie flower) } employed for perfume.
Michelia champaca, L. (champaca) }
Hibiscus sabdariffa.
Lawsonia alba (henna).
Arto-carpus integrifolia (Jak-wood).
Kamela.
Morinda citrifolia, *M. umbellata*, L., *M. bracteata*, Roxb. (Bancudo).
Pterospermum niveum Vid (red-brown).
Narrawood (*Pterocarpus spp.*).

* Brooks, Philippine Journal of Science, 1910, 439.

BRITISH PLANTS CAPABLE OF DYEING MORDANTED WOOL, according to C. B. Plowright (Journ. Roy. Horticultural Society, xxvi., 1901).

Name.	Part Employed.	Colour Obtained.
Anthemis tinctoria	—	Yellow
Anthriscus sylvestris	—	Greenish-yellow
Anthyllis vulneraria	Flowers	Golden-yellow
Arctostaphylos uva-ursi	Leaves	Yellow
Alnus glutinosa	Catkins	,,
Berberis vulgaris	Root bark	,, *
Betula alba	Leaves	,,
Bidens tripartita	Plant	Orange
Caltha palustris	—	Pale yellow
Comarum palustre	—	Red-brown
Cornus sanguinea	Berries	Dull yellow
Chrysanthemum segetum	Flowers	,,
Calendula officinalis	,,	Pale yellow
Calluna vulgaris	Plant	Brown-yellow
Caltha palustris	Flowers	Yellow
Carpinus betulus	Bark	Dull yellow
Chaerophyllum sylvestre	—	Yellow
Empetrum nigrum	Fruit	Mauve
Fraxinus excelsior	Bark	Dull yellow
Genista tinctoria	Plant	Yellow
Genista anglica	Flowers	,,
Galium verum	Rhizome	Red-brown
Humulus lupulus	Young tips	Yellow
Hypericum perforatum	—	Dull yellow
Isatis tinctoria	Plant	Blue *
,, ,,	Flowers	Yellow
Iris pseudacorus	Rhizome	Brown
Juglans regia	Fruit	,, *
Lecanora tartarea	—	Red-violet *
Lycopus europæus	Berries	Green
Ligustrum vulgare	,,	,,
Myrica gale	Plant	Dull yellow
Nymphæa alba	Rhizome	Brown
Origanum vulgare	—	Yellow
Potentilla tormentilla	—	—
Phragmites communis	Flowers	Green
Pyrus malus	Inner bark	Fine yellow
Pyrus communis	Leaves	Yellow
Polyporus hispidus	Fungus	Yellow-brown
Polygonum persicaria	—	Yellow
Polygonum hydropiper	—	,,
Parmelia caperata	Lichens	Brown *
Parmelia saxatilis	,,	,,
Parmelia physodes	,,	,,
Parmelia borreri	,,	,,
Physcia flavicans	,,	Pale yellow-brown *
Physcia parietina	,,	Pale brown *
Prunus spinosa	Fruit	Drab
Quercus robur	Bark	Pale red-brown

* Without mordant.

Name.	Part Employed.	Colour Obtained.
Reseda luteola	Plant	Yellow
Rhamnus catharticus	Berries	,,
Rhamnus frangula	Bark	Orange-brown
Rubus fruticosus	Fruit	Slaty-blue
Rumex acetosa	Roots	Pale yellow
Rumex crispus	,,	,,
Rumex obtusifolius	,,	,,
Spiræa ulmaria	Rhizome	Red-brown
Stachys sylvatica	—	Dull yellow
Stachys palustris	—	Pale yellow-brown
Scabiosa succisa	—	Dull yellow
Sambucus nigra	Berries	Violet
Senecio jacobæa	Plant	Good yellow
Serratula tinctoria	—	Yellow
Salix cinerea	Leaves	Pale yellow-brown
Salix triandra	,,	Yellow
Thalictrum flavum	—	Poor yellow
Trifolium pratensis	Flowers	Pale yellow
Tanacetum vulgare	—	Yellow
Tormentilla officinalis	Rhizome	—
Ulex europæus	Flowers	Straw-yellow
Urceolaria scruposa	Lichen	Orchil colour *
Umbilicaria polyphylla	,,	,,
Xanthium strumarium	Plant	Yellow

* Without mordant.

LEAVES AND FLOWERS OF WILD AND CULTIVATED BRITISH PLANTS CAPABLE OF DYEING ALUMINIUM MORDANTED COTTON, according to Unpublished Experiments by the late Professor J. J. Hummel.

Wild.

Plant.	Flower.	Leaf.	Colour Obtained.
Acer campestre	—	L.	Dull yellow
Acer pseudo-platanus	—	,,	,, ,,
Achillea ptarmica	F.	,,	,, ,,
Alliaria officinalis	,,	—	Pale yellow
Alnus glutinosus	—	L.	Brown-yellow
Anthyllis vulneraria	F.	—	Bright yellow
Arum maculatum	—	L.	,, ,,
Bellis perennis	F.	—	,, ,,
Calluna vulgaris	Young shoots	—	Orange-yellow
Caltha palustris	F.	—	Yellow
Campanula rotundifolia	,,	—	Pea-green
Carex dioica	—	—	Orange-brown
Caucalis anthriscus	F.	L.	Yellow
Centaurea nigra	,,	—	Pale yellow
Centaurea cyanus	—	L.	Dull yellow

Plant.	Flower.	Leaf.	Colour Obtained.
Chærophyllium sylvestre	F.	—	Bright yellow
Cheiranthus cheiri	,,	—	Green-yellow
Chrysanthemum segetum	—	L.	Orange-yellow
Colchicum autumnale	F.	—	Bright yellow
Corylus avellana	,,	—	Dull brown-yellow
Cratægus oxyacantha	,,	—	Dull yellow
Daucus carota	,,	—	Pale dull yellow
Digitalis purpurea	,,	—	Yellow
Draba verna	—	—	Pale dull yellow
Epilobium tetragonum	F.	L.	Yellow
Erica cinerea	,,	—	Pale dull yellow
Erica tetralix	—	L.	Dull yellow
Euphorbia helioscopia	F.	,,	Yellow
Euphorbia peplus	,,	,,	Bright yellow
Fagus sylvatica	—	,,	Dull purple
Fragaria vesca	—	,,	Yellow
Geranium sylvaticum	F.	,,	Dull yellow
Geranium pratense	,,	,,	,, ,,
Geranium lucidum	—	,,	Brown-yellow
Helleborus viridis	F.	,,	Pale yellow
Heracleum sphondylium	,,	—	Bright yellow
Humulus lupulus	,,	—	Pale brown-pink
Hydro-cotyle vulgaris	—	L.	Yellow
Iris pseudacorus	F.	—	Pale yellow
Lapsana communis	—	L.	Pale brown-yellow
Lathyrus pratensis	F.	,,	Yellow
Leontodon autumnalis	,,	—	Pale yellow
Lonicera periclymenum	,,	—	Pale dull yellow
Lotus corniculatus	,,	L.	Orange-yellow
Mentha aquatica	,,	—	Dull yellow
Mercurialis perennis	,,	L.	Pale dull yellow
Myosotis palustris	,,	,,	Pale brown
Narcissus pseudonarcissus	,,	—	Pale bright yellow
Narthecium ossifragum	,,	—	Pale yellow
Parnassia palustris	,,	—	Dull yellow
Pimpinella saxifraga	,,	—	,, ,,
Plantago major	—	L.	,, ,,
Polygonum aviculare	Plant	—	Pale brown-yellow
Polygonum persicaria	F.	—	Dull brown-yellow
Populus alba	—	L.	Bright yellow
Potentilla tormentilla	Plant	—	Dull yellow
Potentilla anserina	F.	L.	,, ,,
Primula veris	F., red	—	Yellow
Primula veris	F., yellow	—	Dull brown-yellow
Prunus padus	—	L.	Brown-yellow
Quercus robur	—	,,	Dull yellow
Ranunculus acris	F.	—	Dull green-yellow
Ribes grossularia	Bark and root	—	Dull brick-red
Rubus fruticosus	F.	—	Dull yellow
Rubus fruticosus	Fruit	—	Violet
Rumex sanguineus	—	L.	Dull yellow
Sagina procumbens	Plant	—	Pale yellow
Sambucus nigra	F.	L.	Pale dull yellow
Sambucus nigra	Fruit	—	Red-violet
Sarcothamnus scoparius	F.	—	Dull yellow
Saxifraga tridactylites	Plant	—	,, ,,

Plant.	Flower.	Leaf.	Colour Obtained.
Saxifraga umbrosa	F.	—	Brown-yellow
Senecio jacobæa	,,	L.	Yellow
Taraxacum dens leonis	,,	—	Pale yellow
Teucrium scorodonia	—	L.	' Yellow
Thymus serpyllum	Plant	—	Dull brown-yellow
Trifolium pratense	F.	L.	Yellow
Trifolium repens	—	,,	,,
Ulex europæus	F.	—	Orange-yellow
Veronica beccabunga	Plant	—	Dull yellow
Viburnum opulus	F.	L.	Pale dull yellow
Viola canina	,,	—	Brown-yellow
Viola tricolor	,,	—	Pale yellow

Cultivated.

Plant.	Flower.	Leaf.	Colour Obtained.
Aster amellus var. bessarasicus	F.	—	Dull yellow
Aster nova angulé roseus	,,	—	,, ,,
Æsculus hippocastanum	—	L.	,, ,,
Antirrhinum (plum coloured petals)	F.	—	Yellow-olive
Bocconia cordata (white)	,,	—	Pale dull yellow
Centaurea cyanus	,,	—	,, ,, ,,
Careopsis grandiflora	Yellow petals	—	Bright orange
Dahlia (huntsman)	Orange ,,	—	Orange-yellow
Dahlia (Maid of Kent)	Red ,,	—	Dull orange-yellow
Dahlia helichrysum	F.	—	Olive-yellow
Dahlia (white button)	,,	—	Yellow
Dahlia (Sidney Hollings)	Dark purple petals	—	Dull blue-green
Doronicum austriacum	F.	L.	Pale dull yellow
Erigeron speciosus	Yellow florets	—	Yellow
Euphorbia jacquiniflora	F.	—	Dull blue-pink
Forsythia pendula	,,	—	Yellow
Fuchsia alexandrina	F., white petals	—	,,
Fuchsia alexandrina	Red sepals	—	Brown-pink
Fuchsia (crimson bedder)	,, petals	—	Yellowish-green
Fuchsia globosa	,, ,,	—	Pale olive
Fuchsia oxoniensis	Red-purple petals	—	Pale yellow
Genista prostrata	—	L.	Yellow
Helianthus rigidus	F.	—	Pale brown-yellow
Helenium autumnale	,,	—	Yellow
Hollyhock	—	—	—
Juniperus sabina	—	L.	Dull yellow
Lilium speciosum kratzeri	Anthers	—	Pale dull yellow
Nicotiana affinis	F.	—	Very pale ,,
Phlox drummondi	,,	—	Bright yellow
Polygonum brunonis	,,	—	Dull brown-violet
Prunus pisardi	—	L.	,, ,,
Potentilla argyrophylla	F.	—	Dull brown-olive

Plant.	Flower.	Leaf.	Colour Obtained.
Salvia pratensis var. baumgarteni	F.	—	Pale dull violet
Tagetes patula	„	—	Old gold shade
Tropæolum majus . . .	—	L.	Yellow
Vitis vitifera	Purple skin	—	Purple, somewhat pale
Viola (skylark)	F.	—	Yellow
Viola (Ardwell gem) . . .	„	—	„
Viola (Holyrood)	„	—	Pale green-yellow

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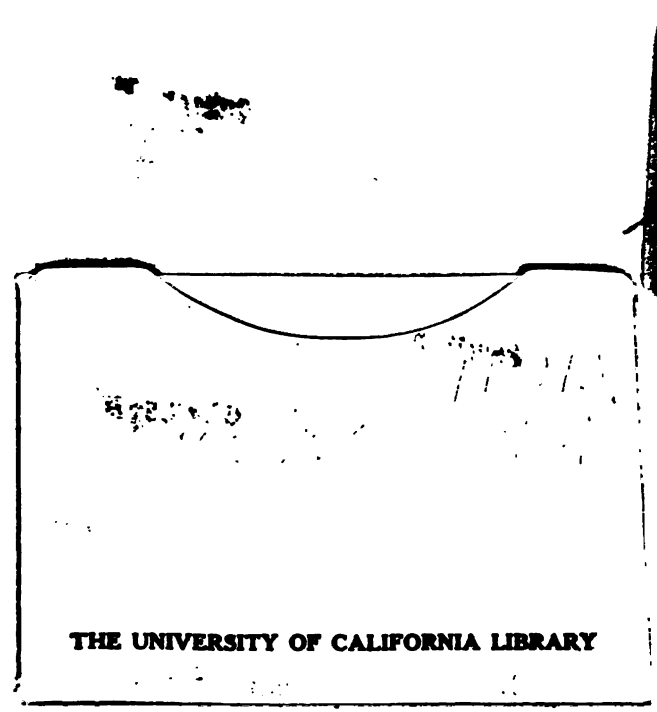
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